

CHEMISTRY FOR CAPE

**2018
EDITION**

by Susan Maraj

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**2018
EDITION**

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Chemistry for CAPE 2018 Edition

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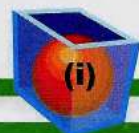
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Section 4

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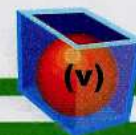
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Section 6
Industry and the Environment

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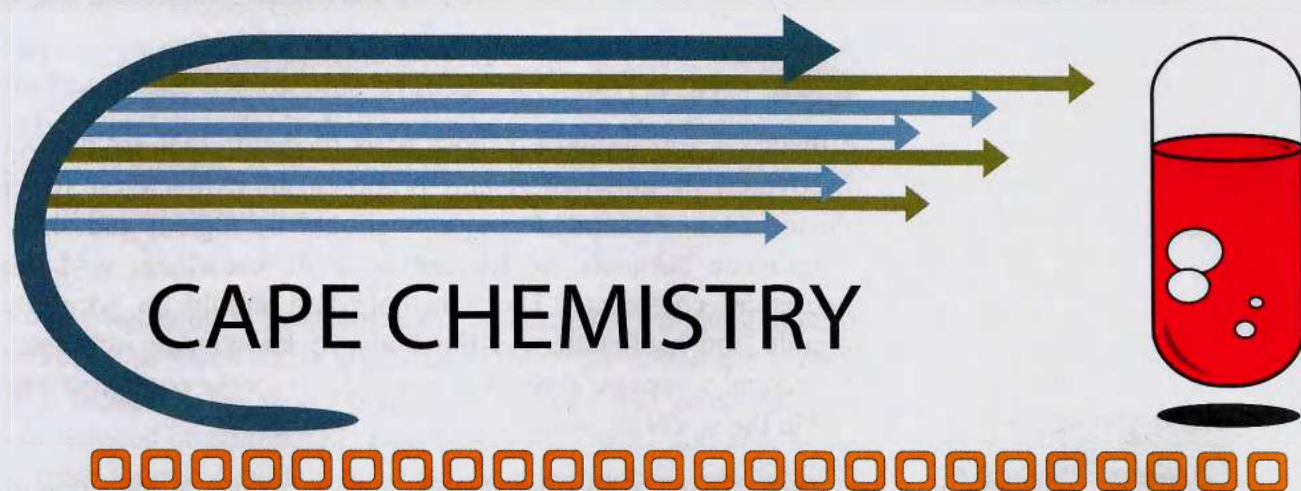


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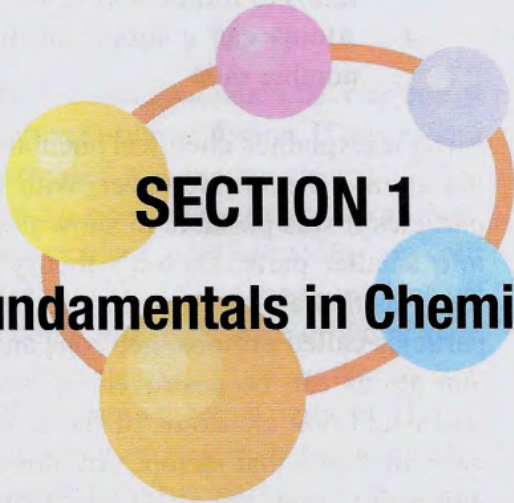
FOR CAPE

by

SUSAN MARAJ AND ARNOLD SAMAI



CAPE CHEMISTRY

A graphic of a molecular model with four colored spheres (yellow, pink, light blue, and orange) connected by an orange ring.

SECTION 1

Fundamentals in Chemistry



THE ATOMIC THEORY

A theory is substituted for those parts of reality that are not yet discovered or understood and proposes an explanation for a phenomenon. Acceptable theories should be logical and show congruence between the present body of knowledge and the theoretical constructs. The data collected should be accurate, reliable and replicable. As the body of knowledge increases, theoretical adjustments must be made to overcome contradictions within the scientific society.



John Dalton

In 1808, John Dalton developed the first useful atomic theory of matter. Although some of the details of his atomic theory are now known to be incorrect, the basic concepts are foundations of modern science.

Dalton's atomic theory made the following assumptions:

- Matter consists of small particles called atoms
- Atoms are indestructible or indivisible
- Atoms of the same elements are identical in mass and properties
- Atoms combine chemically in simple whole number ratios to form compounds
- Atoms can combine in more than one simple whole number ratio

Many unexplained chemical phenomena soon became clear using his atomic theory. However, with the discovery of subatomic particles it was possible to show that the atom could be divided into smaller parts. Dalton's theory had two major errors. The first was that atoms could indeed be sub-divided into subatomic particles called protons, neutrons and electrons. It is also known that atoms can be destroyed by nuclear reactions. Dalton also postulated that all atoms of the same element are identical and we now know that isotopes of atoms exist and as such they are indeed different. We also know that atoms of the same element can have different masses as seen in isotopes.



Discovery of subatomic particles

J.J. Thomson

In 1897 Thomson deflected cathode rays with both electric and magnetic fields. He reasoned that, if a particle had momentum, it must have a mass, thus cathode rays must be a stream of particles. He used the results to measure the charge to mass ratio and found these particles to be negatively charged and had a mass nearly 2000 times lighter than the mass of a hydrogen atom. Thomson proved the existence of electrons. His work made it apparent that atoms were not indivisible and it gave evidence for the existence of subatomic particles. He proposed the 'plum pudding' model of the atom which described atoms as negative charged electrons embedded in a sphere of positive charge.

E. Goldstein

In 1900 Goldstein discovered protons after observing the rays in a cathode-ray tube that were travelling in the direction opposite to that of the cathode rays. According to Goldstein, since atoms are electrically neutral they must contain equal number of positively charged particles as negatively charged particles.

Ernest Rutherford

In 1909, Rutherford's colleagues Geiger and Marsden bombarded thin metal foils with alpha particles to test Thomson's model of the atom. They found that most of the alpha particles passed straight through the foil, showing that they must have passed through essentially empty space. However a small portion of the alpha particles were deflected at very large angles, and a few even bounced back towards the source. This indicated that strong forces were present to cause deflection of the alpha particles. Rutherford proposed that most of the atom must be mainly empty space with the mass and positive charge being concentrated in a tiny central nucleus while the electrons orbit the nucleus like the planets orbit the Sun. Rutherford's planetary model of the atom did not explain why the negative electron revolving a positive nucleus did not lose energy and spiral into the nucleus or what prevented the electrons from being pulled into the nucleus by electrostatic attraction.

Niels Bohr

In 1913 Bohr proposed an atomic model based on the quantum theory in which electrons move around the nucleus in definite orbits. He worked out that the electrostatic force between the nucleus and an orbiting electron was cancelled out by the outward



J.J. Thomson





H. Moseley

force due to orbital motion. Bohr suggested that an electron in a given orbit can have only a certain amount of energy and the orbit can have only a certain radius. If the electron absorbs a quantum of energy, it moves to an orbit with a higher energy level which is further away from the nucleus. The electron becomes excited and emits energy to return to its stable orbit.

Henry Moseley

In 1913 Moseley suggested that if atoms are neutral, then the number of electrons must be the same as the number of protons. Since electrons have negligible mass, and atomic masses are greater than the mass of protons in the atom then the extra mass must be the existence of a particle with mass but no charge. Rutherford also put forward this idea and called the particle a neutron. Thus began the search for the neutron.

James Chadwick

In 1932 Chadwick bombarded the element Be with alpha particles. This produced a highly penetrating stream of particles, which could pass through many centimeters of solid lead and which was not deflected by electric or magnetic fields. He had detected the neutron.



ATOMIC STRUCTURE

The word 'atom' comes from the Greek 'atomos' which means something that cannot be split into smaller pieces. Atoms are considered the basic building blocks of Chemistry.

Atoms consist of protons, electrons and neutrons. The protons and neutrons are held in a tiny nucleus by powerful nuclear forces while the electrons are found orbiting the nucleus. The mass of the subatomic particles is measured relative to one twelfth the mass of a carbon-12 isotope, while the charge of the particles is compared to the charge of a proton and an electron. A proton has a relative charge of +1 and a relative mass of 1. A neutron has no charge and a relative mass of 1. An electron has a relative charge of -1 and negligible mass ($\frac{1}{1837}$ of a proton).

Table 1.1

The relative masses, charges and positions of protons, electrons and neutrons within the atom

Particles	Mass	Charge	Position
Proton	1	+1	In the nucleus
Neutron	1	0	In the nucleus
Electron	$\frac{1}{1837}$	-1	Orbiting the nucleus

Experiments in which subatomic particles are deflected in electric and magnetic fields show that electrons are deflected at large angles towards the positive pole while protons are deflected at smaller angles towards the negative pole and neutrons showed no deflection. This suggests that electrons are negatively charged particles and lighter than protons while protons are positively charged particles. The fact that neutrons were not deflected by either electric or magnetic fields suggests that these particles do not carry an electric charge and are therefore neutral.

Fig. 1.1

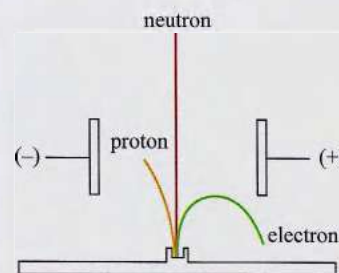


Fig. 1.1

Behaviour of particles in an electric field

Atomic number, mass number, isotopes

Since atoms are electrically neutral species, the number of protons must be equal to the number of electrons. The number of protons in the nucleus of an atom is called the **atomic number** or **proton number**. Atoms of the same element have the same number of protons and hence the atomic number is used to define the atom. Each atom has an **atomic mass** or **mass number** which is the sum of the protons and neutrons in the nucleus of the atom. Since the protons and neutrons are found in the nucleus of the atom, the atomic mass is also referred to as the *nucleon number*.

In 1913 Thomson found that some atoms of the same elements had different masses. He discovered the existence of **isotopes** which are atoms with the same atomic number but different mass numbers. Isotopes of an element have the same atomic number because they have the same number of protons but the difference in mass numbers is due to the different numbers of neutrons present. Since the number of protons is equal to the number of electrons, isotopes have identical chemical properties however their physical properties are different because they have different masses. Most elements consist of more than one isotope. For example, chlorine exist with mass number 35 and 37. Chlorine-35 contains 17 protons and 18 neutrons while chlorine-37 contains 17 protons and 20 neutrons. The proportion of each isotope in



a given element is called the **relative abundance**. The relative abundance is the ratio or percentages in which they exist in the world. If the relative abundance is minute and is insignificant it is not considered in calculating the relative atomic mass for placement in the Periodic Table. It is no surprise that although isotopes of some elements exist, the relative atomic masses are whole numbers whereas there are some whose masses are not whole numbers. The mass of an element depends on the relative abundance of the isotopes present in the element.

Relative atomic and isotopic masses

The actual mass of an atom is so small that it is not practical to work with therefore a reference is used and compared to the actual atomic mass. In 1961 it was agreed internationally that the carbon-12 isotope should be used as the reference. The mass of an atom relative to (compared to) the reference is called the **relative atomic mass** which is the mass of an atom compared to one twelfth the mass of a carbon-12 isotope. The relative atomic mass is not usually a whole number because the average weight and relative abundance of the isotopes of elements in naturally occurring samples are measured. The **relative isotopic mass** is the mass of a single isotope compared to one twelfth the mass of a carbon-12 isotope.



MASS SPECTROMETER

In 1919, F. Aston developed the mass spectrometer which was used to measure the mass and relative abundance of each isotope in a sample of naturally occurring element.

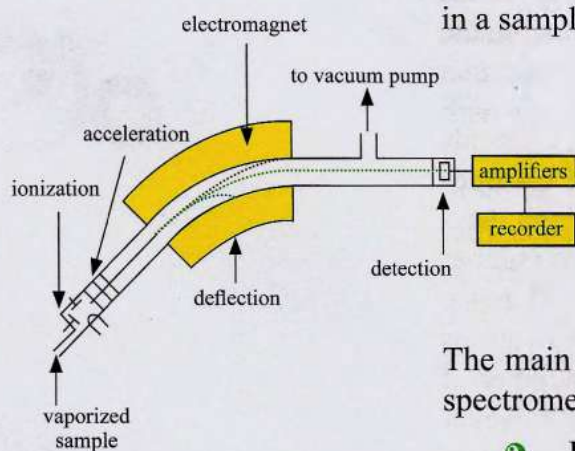


Fig. 1.2

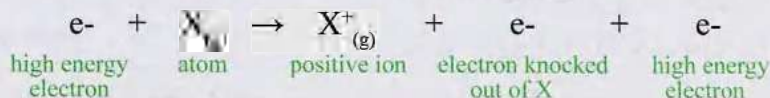
Diagram showing how the mass spectrometer works

Fig. 1.2

The main steps involved in the operating principles of the mass spectrometer are:

- 1. **Ionization.** The sample of the element is vaporized and injected into the instrument. The element passes into the ionization chamber where the atoms are bombarded by a beam of high energy electrons which knocks one or more electrons out of the atoms converting them into

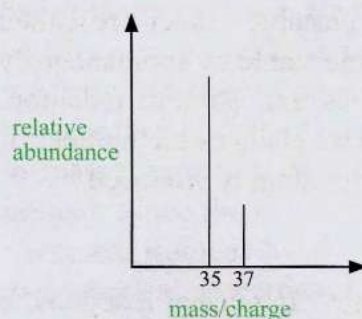
positively charged ions. For example



- **Acceleration.** The positive ions move into the accelerating chamber where an electric field accelerates positive ions towards a magnetic field.
- **Deflection.** The fast moving ions are deflected according to their mass and charge as they pass through the magnetic field. Ions with lower mass to charge ratios are deflected more than ions with higher mass to charge ratios.
- **Detection.** The ions are detected by an instrument which is attached to an amplifier and a recorder. When the accelerating electric field and the magnetic field are kept constant, only ions of a specific mass to charge ratio can be detected. Higher or lower mass to charge ratios are either deflected too little or too much to make contact with the detector. Therefore by varying the electric field and magnetic field strength, one isotope after another can be deflected to hit the detector. The mass and the relative abundance of each isotope can be measured and an accurate value for the relative atomic mass can be calculated. The relative heights of the peaks produced by the recorder give a measure of the relative abundance of the different isotopes present.

Example

The mass spectrum of chlorine atoms shows the relative abundance of chlorine-35 is 75.8% and chlorine-37 is 24.2%. Calculate the relative atomic mass (A_r) of chlorine.



$$\begin{aligned} A_r &= \frac{75.8}{100} \times 35 + \frac{24.2}{100} \times 37 \\ &= 35.5 \end{aligned}$$





RADIOACTIVITY

Discovery of radioactivity



X-ray of a hand



Pierre and Marie Curie

In 1903, Henri Bacquerel was awarded the Nobel Prize for Physics for his discovery of radioactivity. Bacquerel wrapped uranium covered photographic plates in black paper and placed them in a drawer for a few days. He found that clear images were developed on the plates which suggested that uranium emitted radiation. He later showed that the radiation emitted were not only similar to X-rays and could also be deflected by a magnetic field which suggests that they consist of charged particles.

Pierre and Marie Curie were interested in the recent discovery of radiation and conducted research on radioactive substances. They found that uranium ore contained much more radioactivity than could be explained by the uranium content alone. The Curie's research led them to the discovery of the radioactive elements radium and polonium. They shared the Noble Prize for Physics with Bacquerel in 1903. After Pierre's accidental death, Marie continued her own research and received a second Noble Prize in 1911 for chemistry for her isolation of radium. Her research in radioactivity was immediately applied to the treatment of cancer and other diseases.

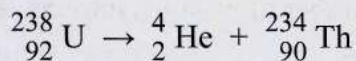
Radioactive isotopes

In the nucleus, a strong nuclear force of attraction exists between nucleons. The neutrons are intimately involved in this attractive force. As the number of protons increases in the atom the positive charges in the nucleus repel each other so that the number of neutrons needed to create a stable nucleus increases more rapidly than the number of protons. However, even with an increasing number of neutrons to protons in the nucleus, nuclei with 84 or more protons are unstable. The unstable nuclei are called radioactive isotopes. The nuclei become stable by spontaneously ejecting alpha particles, beta particles and gamma radiation. The emission of alpha and beta particles changes the number of protons in the nucleus so that a different atom is produced.

Alpha particles

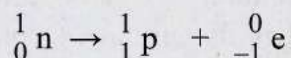
Alpha particles are helium nuclei, ${}^4_2\text{He}^{2+}$. In nuclear reactions, it is understood that alpha particles are formed without its electrons therefore the symbol ${}^4_2\text{He}$ is used in nuclear equations. The emission of alpha particles leads to a decrease in atomic number

by 2 and mass number by 4.

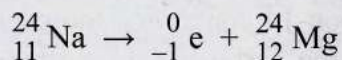


Beta particles

Beta particles are formed when a neutron disintegrates giving a proton and an electron.



The proton remains in the nucleus of the atom, so its atomic number increases by 1. The mass number is unchanged.



Gamma rays

Gamma rays are electromagnetic waves of short wavelength. Emissions of alpha or beta particles are often accompanied by the emission of gamma rays. When particles are emitted, the atomic nucleus becomes excited and the excess energy is released as gamma radiation for the nucleus to return to a more stable energy level.

Band of stability

Repulsion between the positive charges of the protons is minimized by the presence of neutrons in the nucleus. As the atomic number of an element increases, the neutron to proton ratio must also increase to keep the nucleus together. In larger atoms, even the increasing number of neutrons is not enough to keep the nucleus together and the nucleus becomes unstable.

A plot of the number of neutrons against the number of protons in stable nuclei shows that stable nuclei are located in a shaded area of the graph known as the band of stability. The majority of radioactive nuclei occur outside this band.

Fig. 1.3

The type of radioactive decay that a particular radioisotope undergoes depends to a large extent on its neutron to proton ratio compared to those of nearby nuclei within the band of stability. Nuclei above the band of stability which have a high neutron to proton ratio can move towards the band of stability by emitting a beta particle and thus increasing the number of protons in the nucleus.

Heavy nuclei which have atomic number greater than 84 tend

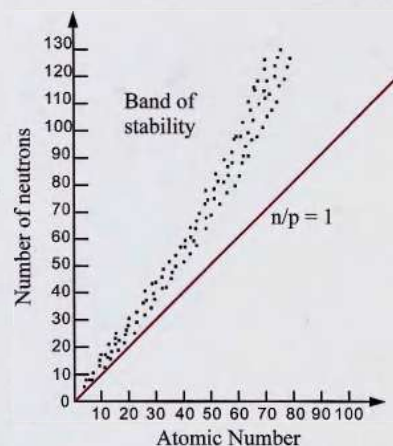


Fig. 1.3

Graph showing the band of stability



to undergo alpha emission. This decreases both the number of neutrons and the number of protons, moving the nucleus towards the band of stability.

Uses of radioisotopes

Carbon-14 dating

All living organisms contain a given concentration of carbon-14, when the organism dies its carbon-14 concentration decreases due to radioactive decay. We can use this information to tell when the organism died. It works like this, when an organism dies it has a specific ratio by mass of carbon-14 to carbon-12 in its body. No new carbon-14 containing molecules are metabolized after death so that the carbon-14 to carbon-12 ratio begins to decrease because carbon-14 is decaying away at a constant and predictable rate. Since the half-life of carbon-14 is 5700 years, then after 5700 years half as much carbon-14 remains within the organism. This dating method using carbon-14 is only good for organisms or artifacts that are biological in nature and that are tens of thousands of years old.



Carbon-14 dating used for the Dead Sea Scrolls

Medical applications

There are many uses of radioisotopes in medicine. Some of these are given below:

- Sterilization of surgical equipment using high-energy gamma rays.
- Radioisotopes are used to locate cancerous tumors and other medical problems. For example iodine-131, a radioisotope of iodine-127 is used to detect thyroid problems. If the thyroid is not absorbing iodine properly the gamma rays emitted by iodine-131 would be detected.
- Bone imaging is another important use of radioisotopes. This technique is good for arthritic patients and bone abnormalities. The patient is injected with Technetium-99 which emits gamma rays and has a half life of six hours. After several hours the patient undergoes bone imaging which shows up any abnormalities on the bone image scan.
- External irradiation to control cancerous growth using a gamma beam from a radioactive cobalt-60 source.
- Internal radiotherapy is probably the most successful kind of cancer treatment. It is done by administering or planting a small radiation source, usually a gamma or beta emitter, in the target area. Iodine-131 is commonly

used to treat thyroid cancer and iridium-192 implants are used especially in the head and breast.

Radioactive tracers

Radioactive tracers can be used in the industry to locate leaks in pipes in much the same way as they are used to find tumors in medicine. The radioisotope is injected into the pipe and a detector is used to locate the leak. The reading on the detector increases closer to the leak as the radiation can escape through the hole in the pipe more easily.

Food irradiation

Food irradiation is a method used to sterilize food using gamma radiation to increase its shelf-life. The result is that the growth of disease-causing micro-organisms or those that cause spoilage are reduced or eliminated. This makes food safer and also keeps it fresh longer. A widely used radioisotope in food irradiation is cobalt-60. The radiation that passes through the food is enough to destroy many disease-causing bacteria as well as those that cause food to spoil, but is not strong enough to change the quality, flavour or texture of the food. The food never comes in contact with the radioisotope and is not at risk of becoming radioactive. Irradiation is most widely used on spices, herbs and dehydrated vegetables. These items are grown in or on the ground and are exposed to naturally occurring pathogens. Some meats are also irradiated. Pork, for example, is irradiated to control the trichina parasite that lives in the muscle tissue of some pigs. Poultry is irradiated to eliminate bacterial contamination.

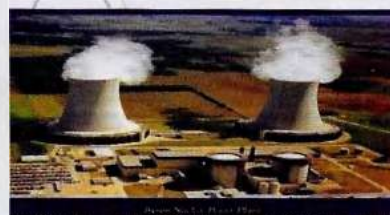
Energy

A tremendous amount of energy is released when the nucleus of an atom is split apart. This is termed **nuclear fission**. If this energy is let out slowly, it can be harnessed to generate electricity. If it is let out all at once, it can make a tremendous explosion as in an atomic bomb. In a nuclear power plant, uranium atoms are split apart in a controlled chain reaction. This chain reaction gives off heat energy which is used to boil water in the core of the reactor. The water from around the nuclear core is sent to another section of the power plant where it heats another set of pipes filled with water to make steam. The steam is used to turn a turbine which can generate electricity. The reaction also produces radioactive material which must be properly disposed off.

Another form of nuclear energy is called **nuclear fusion**. Fusion means joining smaller nuclei to make a larger nucleus. This is



Irradiated ground beef



A nuclear plant





observed in the sun where nuclear fusion of hydrogen atoms into helium atoms takes place. Scientists are still encountering difficulties in controlling nuclear fusion reactions to produce electricity. However, one advantage of nuclear fusion is that it creates less radioactive material than fission.

Disposal of nuclear waste

It is important to our future generation to dispose of nuclear wastes in an efficient way which will not lead to environmental problems or harm the public. There are options developed which have its own positives and negatives.

Underground Disposal

One of the best options for the disposing of highly radioactive wastes is underground. Underground waste disposal is a practical option because it keeps the public safe from radiation. However the area must be secured to keep the materials out of the hands of intruders who would use it for harmful purposes. The radioactive waste is stored in a deep underground facility called a geographic repository.

Space Disposal

This would be done by launching the containers full of waste into space. However the risk of an accident during the launch of the waste makes this option inappropriate.

Ocean Floor Disposal

Scientists have considered burying nuclear waste below the ocean floor. This would prevent the radiation from harming the public and the environment. However, ocean floor disposal poses a problem because apart from being extremely difficult to recover the buried nuclear waste it would also be very difficult to regulate and monitor ocean floor disposal actions.

Ice Sheet Disposal

Nuclear waste disposal has been considered in Polar regions due to its remote location, low population, and stability of thickness of Polar ice. This type of disposal would involve allowing the containers to sink to the bottom of the ice sheet melting its way via its own heat. The containers would be attached to cables to limit their depth as well as allow for easy retrieval. However, future climatic changes such as Polar ice melting could release radioactive wastes into the environment. Also the nuclear waste would have to be transported over great distances leading to possible risks of accidents.

Remote Island Disposal

Remote unpopulated islands have the advantage of being countless miles away from continents. However, ocean transport, especially during bad weather, is a risk to this option. Also other countries may contest the transportation and burial of the waste.

Reprocessing

Some countries can reprocess the used nuclear fuel. This process separates out the uranium and plutonium from the fuel rods. This can help to reduce the total volume of nuclear waste. However the byproduct of this process still needs proper disposal.

When choosing an option for the disposal of nuclear waste it is necessary to consider all the advantages and disadvantages so that a responsible decision can be made for the general welfare of the public as well as the environment.



ARRANGEMENT OF ELECTRONS IN THE ATOM

Atomic spectra

Evidence for the arrangement of electrons in the atom comes mainly from atomic spectra. An atomic spectrum is formed when electromagnetic radiation is absorbed or emitted by an element. Electromagnetic radiation can be viewed as a stream of photons, which are particles with no mass each travelling in a wave-like pattern and moving at the speed of light. Each photon contains a certain quantum of energy and is related by the Planck's equation which indicates the energy is directly proportional to the frequency of the radiation.

$$E = h\nu$$

where E is the energy, ν is the frequency and h is the Planck's constant (6.63×10^{-34} J-sec).

Since the frequency and wavelength of electromagnetic radiation is related by

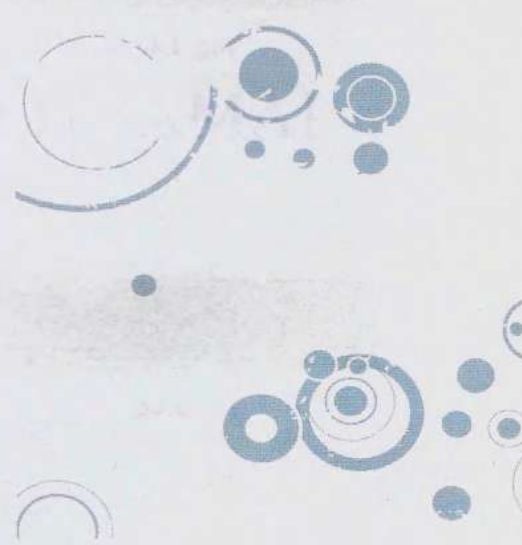
$$c = \nu\lambda$$

where c is the speed of electromagnetic radiation in vacuo (3×10^8 ms⁻¹), ν is the frequency and λ is the wavelength,

Then

$$E = hc/\lambda$$

Thus, a quantum of energy absorbed or emitted by an atom can



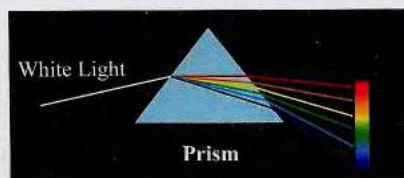


Fig. 1.4a

Formation of a continuous spectrum



Fig. 1.4b

A continuous spectrum



Fig. 1.4c

An absorption spectrum



Fig. 1.4d

An emission spectrum

be determined by measuring the frequency or wavelength of the electromagnetic radiation absorbed or emitted. The whole range of frequencies of the electromagnetic radiation is called the **electromagnetic spectrum**. The absorption or emission of energy by an element corresponds to specific points on the electromagnetic spectrum and produces a unique spectrum which may be used to identify the element.

Fig. 1.4a

If a beam of white light is passed through a prism on to a screen, a spectrum of colours made up of all wavelengths of visible light is seen like in a rainbow. This is called a **continuous spectrum**. There is no distinct division between the colours as they blend in from one to another.

Fig. 1.4b

If white light passes through a substance, the atoms can absorb light of certain wavelength and dark lines appear in the spectrum. A line spectrum is formed which appears as distinct lines and not bands of colours. It is called a **discontinuous spectrum**. The wavelengths of the dark lines in the spectrum are the wavelengths of the light absorbed by the atoms. This line spectrum is an **absorption spectrum**. The absorption of energy by an element corresponds to specific wavelengths on the electromagnetic spectrum and produces a unique spectrum.

Fig. 1.4c

If atoms are supplied with heat or electrical energy to high enough temperatures, they emit energies of certain wavelengths as the excited atoms return to their ground state (stable orbit). An **emission spectrum** is produced which shows coloured lines on a dark background. The emission of energy by an element also corresponds to specific wavelengths on the electromagnetic spectrum and produces a unique spectrum.

Fig. 1.4d

The emission spectrum of hydrogen

The study of the emission spectrum of hydrogen shows that electrons in an atom can exist only in discrete energy levels. According to Bohr, when energy is added to the atoms, an electron in the ground state absorbs a quantum of energy and moves to an orbit with a higher energy level which is further away from the nucleus. This excited electron in the higher energy level cannot maintain this position for a long time and it falls back to a lower energy level. As it falls back it emits a quantum of energy which

is equivalent to the difference in the energy levels. The greater the difference in energy levels, the higher the frequency of light emitted. Each line in the emission spectrum of hydrogen therefore corresponds to a definite wavelength which corresponds to a definite frequency and hence a definite quantum of energy thus providing evidence for discrete energy levels within the atom.

► Fig. 1.5

Bohr assigned the energy levels of the electron with the letter n , the value of n being 1 for the lowest energy level (nearest to the nucleus), 2 for the next higher energy level and so on. His number assignment became known as the **principal quantum number**.

► Fig. 1.6

The emission spectrum of hydrogen consists of several series of lines. These lines arise from the transition of electrons from orbit of higher quantum number to orbits of lower quantum number. The series of lines in the visible region of the hydrogen spectrum arise from transitions from orbits with a higher energy level to energy level $n = 2$ and is called the **Balmer series**. Electron transitions to level $n = 1$ from any of the other orbits result in lines in the ultraviolet region of the spectrum and is called the **Lyman series**. In each series, the lines become closer together as the frequency increases until it converges to forms a continuous spectrum. The convergence line corresponds to the transition from an energy level where the electron is lost from the atom and the atom is ionized. Each series of lines is named after its discoverer.

- The **Lyman series** arise from electron transitions from higher energy levels to principal quantum number 1.
- The **Balmer series** arise from transitions from higher energy levels to principal quantum number 2.
- The **Paschen series** arise from transitions from higher energy levels to principal quantum number 3.
- The **Brackett series** arise from transitions from higher energy levels to principal quantum number 4.
- The **Pfund series** arise from transitions from higher energy levels to principal quantum number 5.

► Fig. 1.7

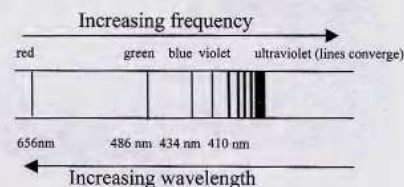


Fig. 1.5
Diagram of the line emission spectrum of hydrogen

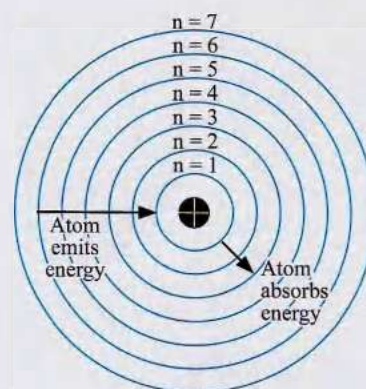


Fig. 1.6
Principal quantum numbers on atom:
The arrow shows the direction the electron moves on absorbing or emitting energy

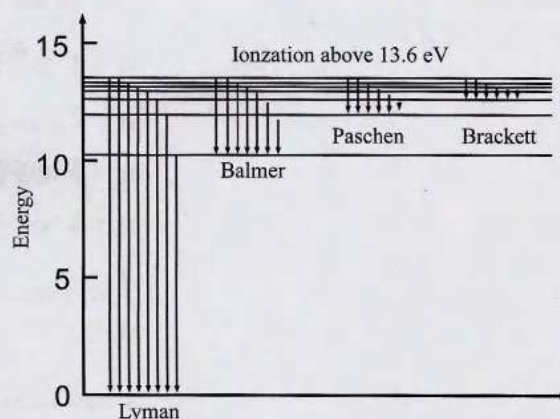


Fig. 1.7
Diagram to show electronic transitions



Quantum numbers

The Bohr's atomic model was one-dimensional and used one quantum number which explained the emission spectrum of hydrogen but failed to explain the spectra of more complex atoms. With the development of **Schroedinger's** wave equation in 1926 which assumes wave-particle duality of electrons, the position of an electron is described in terms of probability density which is the volume of space in which the electron is likely to be found. The region where there is a high probability of finding an electron is called an **orbital**. Schroedinger described an atomic model with electrons in three dimensions and with three quantum numbers. The three quantum numbers are the principal (n), angular (l), and magnetic (m) quantum numbers. These quantum numbers describe the size, shape, and orientation in space of the orbitals on an atom.

The *principal quantum number* n describes the energy level of the electron. It is the same as that used in Bohr's model. The maximum number of electrons in n is $2n^2$.

Energy level	No. of electrons
$n = 1$	2
$n = 2$	8
$n = 3$	18
$n = 4$	32

Table 1.2
Number of electrons in each energy level

The *angular quantum number* l describes the sublevels in n and the shape of the orbitals. The sublevels are given letter designations s, p, d and f. Each energy level has n sublevels.

$n = 1$ has 1 sublevel named 1s

$n = 2$ has 2 sublevels named 2s and 2p

$n = 3$ has 3 sublevels named 3s, 3p and 3d

$n = 4$ has 4 sublevels named 4s, 4p, 4d and 4f

The *magnetic quantum number* m describes the number of orbitals within a sublevel.

s has 1 orbital and can hold up to 2 electrons

p has 3 orbitals and can hold up to 6 electrons

d has 5 orbitals and can hold up to 10 electrons

~~**f** has 7 orbitals and can hold up to 14 electrons~~

A fourth quantum number, s , is used to describe the spin of the electron. According to the **Pauli Exclusion Principle** no more than two electrons can occupy an orbital and two electrons occupying the same orbital must have opposite spins therefore no two electrons in an atom can have the same four quantum numbers.



SHAPES OF ORBITALS

s orbitals

The atomic orbital is the volume of space around the nucleus in which there is a high probability of finding an electron of a given energy. Each energy level has one s orbital which can hold a maximum of 2 electrons. The shape of the s orbital is spherical. The 1s orbital has a zero electron density or **node** at the center of the nucleus. The electron density increases as the distance from the nucleus increases until it reaches a maximum then it steadily falls, but does not reach zero. Therefore the probability of finding an electron at a radius r is the same in all directions. The 2s orbital is similar in shape to the 1s however the electron density is high closer to the nucleus then falls to a node and then increases to a maximum further from the nucleus.

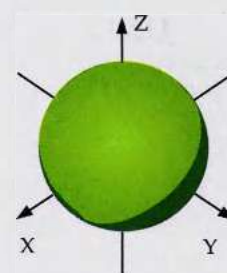


Fig. 1.8a
s orbital

► Fig. 1.8a

p orbitals

Each energy level has three **degenerate** p orbitals i.e. the three p orbitals are of equal energy. Each p orbital is shaped like a dumb-bell and is at right angles to each other. A node exists between each lobe of the orbital. The three 2p orbitals are referred to as the 2p_x, 2p_y and 2p_z orbitals.

► Fig. 1.8b



ELECTRON CONFIGURATIONS

The relative energies of atomic orbitals

There is no difference between the energies of the different sublevels within an energy level for an atom that contains one electron. However, once an atom contains more than one electron, the energy changes in the different sublevels. The s orbital will have a slightly lower energy than the p orbitals at the same energy level, so the s orbital always fills with electrons before the corresponding p orbitals.

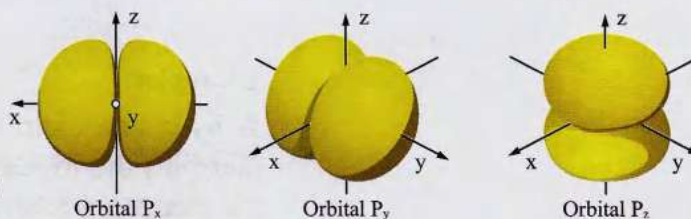


Fig. 1.8b
p orbitals



Within a given energy level, the s orbital will have the lowest energy then the p, d and f.

Relative energies of orbitals are $s < p < d < f$

There is an irregularity in the position of the 3d and 4s orbitals. The 3d orbitals have slightly more energy than the 4s therefore the 4s orbital fills first then the 3d orbitals followed by the 4p orbitals.

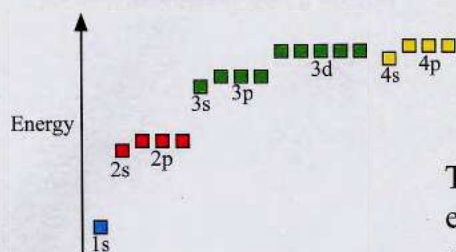


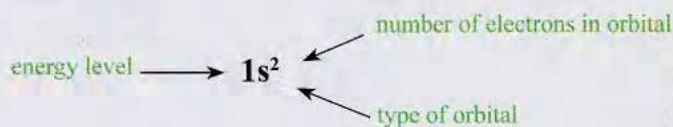
Fig. 1.9
Diagram showing relative energies of orbitals

Fig. 1.9

The **electron configuration** describes the arrangement of electrons in the orbitals of an atom. The electronic configuration can be worked out as follows:

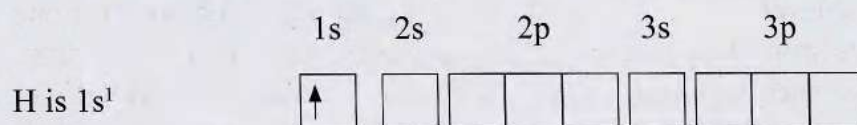
- electrons are added to an atom, one at a time, starting with the lowest energy orbital (**Aufbau principle**)
- no more than two electrons can occupy an orbital (**Pauli exclusion principle**)
- electrons fill degenerate orbitals one at a time with parallel spin before a second electron is added with opposite spin (**Hund's rule**)

The electronic configuration is written with the principal quantum number (1,2,3 etc.) followed by the symbol for the orbital (s, p, d, f) and a superscript which shows the number of electrons in the sublevel.



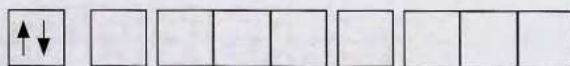
Examples

A hydrogen atom (atomic number 1) has one electron which occupies the lowest energy orbital i.e. the 1s orbital. Therefore the electronic configuration of a hydrogen atom is written as $1s^1$. This can also be represented as 'electrons-in-boxes' which show each orbital as a box and the electrons as arrows in the boxes.



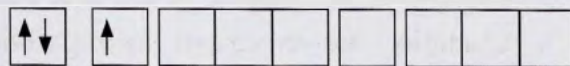
Helium (atomic number 2) has 2 electrons so the second electron also fills the 1s orbital.

He is $1s^2$



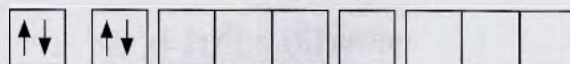
Lithium (atomic number 3) has 3 electrons so the third electron goes into the next lowest energy orbital i.e. the $2s$ orbital.

Li is $1s^2 2s^1$



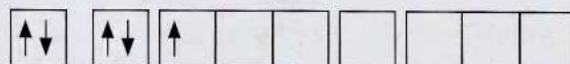
Beryllium (atomic number 4) has 4 electrons so the fourth electron fills the $2s$ orbital.

Be is $1s^2 2s^2$



After the $1s$ and $2s$ orbitals have been filled, the next lowest energy orbitals are the three degenerate $2p$ orbitals. The fifth electron in Boron (atomic number 5) therefore goes into one of these orbitals.

B is $1s^2 2s^2 2p^1$



The sixth electron in carbon (atomic number 6) is added to an unfilled $2p$ orbital

C is $1s^2 2s^2 2p^2$



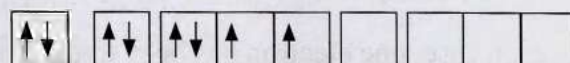
For nitrogen (atomic number 7), the seventh electron is added to the last unfilled $2p$ orbital

N is $1s^2 2s^2 2p^3$



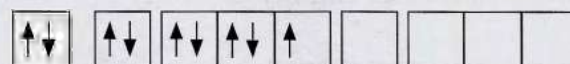
Since each orbital in this sublevel now contains one electron, the eighth electron in oxygen (atomic number 8) fills one of the $2p$ orbitals with electron spin in opposite direction

O is $1s^2 2s^2 2p^4$



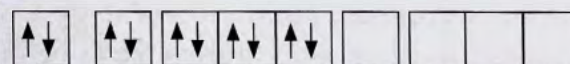
The ninth electron in fluorine (atomic number 9) fills a second orbital in this sublevel

F is $1s^2 2s^2 2p^5$

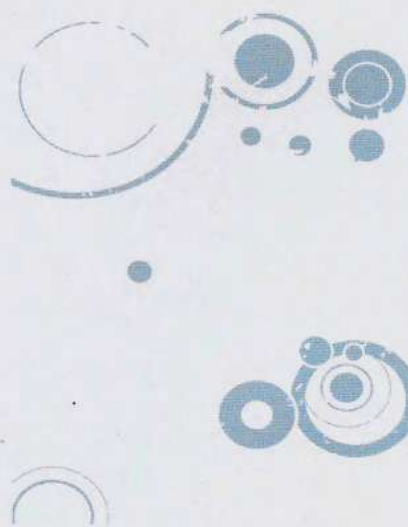


The tenth electron in neon (atomic number 10) completes the $2p$ sublevel

Ne is $1s^2 2s^2 2p^6$



The eleventh electron in sodium (atomic number 11) fills the next lowest energy orbital which is the $3s$ orbital



Na is $1s^2 2s^2 2p^6 3s^1$

↑↓	↑↓	↑↓	↑↓	↑↓	↑			
----	----	----	----	----	---	--	--	--

He and Ne have electronic configurations with filled shells of orbitals. We can use this to write an abbreviated electronic configuration in terms of the previously filled shells of electron. For example, the electronic configuration of Mg (atomic number 12) is $[\text{Ne}] 3s^2$.

The following elements show how the electrons are filled in the 3p orbitals,

Al (atomic number 13) is $[\text{Ne}] 3s^2 3p^1$

Si (atomic number 14) is $[\text{Ne}] 3s^2 3p^2$

P (atomic number 15) is $[\text{Ne}] 3s^2 3p^3$

S (atomic number 16) is $[\text{Ne}] 3s^2 3p^4$

Cl (atomic number 17) is $[\text{Ne}] 3s^2 3p^5$

Ar (atomic number 18) is $[\text{Ne}] 3s^2 3p^6$

Special Electronic Configurations

Once the 3p orbitals are filled, the 4s orbital is filled before the 3d orbitals because the 4s orbital is at a slightly lower energy than the 3d. Therefore

K (atomic number 19) is $[\text{Ar}] 4s^1$

Ca (atomic number 20) is $[\text{Ar}] 4s^2$

Sc (atomic number 21) is $[\text{Ar}] 4s^2 3d^1$

The next 9 elements fill electrons in the 3d orbitals. However there is a little irregularity in the electronic configuration of Cr and Cu.

Cr is $[\text{Ar}] 4s^1 3d^5$ and not $[\text{Ar}] 4s^2 3d^4$

Also Cu is $[\text{Ar}] 4s^1 3d^{10}$ and not $[\text{Ar}] 4s^2 3d^9$

In each case, one electron has been transferred from the 4s orbital to a 3d orbital because the half-filled and filled sublevels of the 3d orbital decreases slightly in energy and spin pairing of the 4s orbital increases slightly in energy.

It must be noted that when a transition metal atom forms an ion, the 4s electrons are lost first. As the 3d orbitals are filled, electron repulsion pushes the 4s electrons further from the nucleus so that the 4s electrons are pushed to an energy level higher than the 3d. Thus the electrons are lost from the 4s before those of the 3d.

Table 1.3

The electron configurations of the elements of atomic number 1 to 30

Atomic Number	Symbol	Electron Configuration
1	H	1s ¹
2	He	1s ² or [He]
3	Li	[He] 2s ¹
4	Be	[He] 2s ²
5	B	[He] 2s ² 2p ¹
6	C	[He] 2s ² 2p ²
7	N	[He] 2s ² 2p ³
8	O	[He] 2s ² 2p ⁴
9	F	[He] 2s ² 2p ⁵
10	Ne	[He] 2s ² 2p ⁶ or [Ne]
11	Na	[Ne] 3s ¹
12	Mg	[Ne] 3s ²
13	Al	[Ne] 3s ² 3p ¹
14	Si	[Ne] 3s ² 3p ²
15	P	[Ne] 3s ² 3p ³
16	S	[Ne] 3s ² 3p ⁴
17	Cl	[Ne] 3s ² 3p ⁵
18	Ar	[Ne] 3s ² 3p ⁶ or [Ar]
19	K	[Ar] 4s ¹
20	Ca	[Ar] 4s ²
21	Sc	[Ar] 4s ² 3d ¹
22	Ti	[Ar] 4s ² 3d ²
23	V	[Ar] 4s ² 3d ³
24	Cr	[Ar] 4s ¹ 3d ⁵
25	Mn	[Ar] 4s ² 3d ⁵
26	Fe	[Ar] 4s ² 3d ⁶
27	Co	[Ar] 4s ² 3d ⁷
28	Ni	[Ar] 4s ² 3d ⁸
29	Cu	[Ar] 4s ¹ 3d ¹⁰
30	Zn	[Ar] 4s ² 3d ¹⁰



IONIZATION ENERGY

First ionization energy of an element is the energy needed to convert one mole of its gaseous atoms into gaseous ions with a single positive charge.

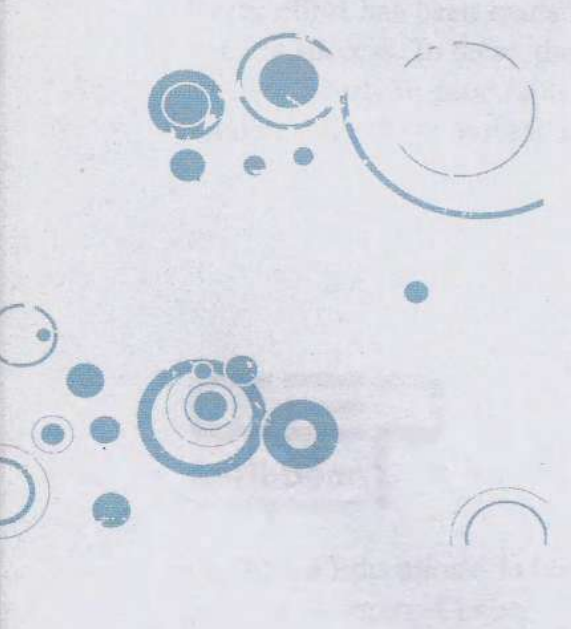




The energy required to remove each successive electron is called the second, third etc. ionization energy. All ionization energies are positive because it requires energy to remove an electron.

Factors influencing the ionization energies of elements

The magnitude of the ionization energy depends on how strongly the electron to be lost is attracted to the nucleus. The attraction may be influenced by the following:

- **The distance the outer electron is from the nucleus.** As the distance between the outer electron and the nucleus increases, the nuclear attraction for the outer electron decreases and the ionization energy decreases.
 - **The size of the nuclear charge.** As the nuclear charge increases, the attraction of the nucleus for the outer electron increases and the ionization energy increases. It must be noted that the atomic radii and electron screening can outweigh the effect of the nuclear charge. For example, in group 1 although Cs has a larger nuclear charge than Na, it loses an electron more readily than Na.
 - **The screening effect of the inner electrons.** Apart from electrons being attracted to the nucleus, they also experience electron repulsion by other electrons. The outer electrons are shielded from the attraction of the nucleus by the repelling effect of the inner electrons. The screening effect of electrons in lower energy levels is more effective than electrons in higher energy levels. Electrons in the same energy level exert negligible screening effect on each other. Therefore as the screening effect of the inner electron becomes more effective, the ionization energy decreases.
- 

Evidence for energy levels

Evidence for discrete energy levels comes from the successive ionization energies required to remove all the electrons from an atom. The successive ionization energies increase since the inner electrons are more strongly attracted to the positively charged nucleus. However, unusually larger increases in ionization energy are observed in the sequence. This large increase usually occurs where all of the electrons in the outer shell are removed and an electron is now being removed from the inner shell.



Successive ionization energies can therefore tell the group the atom is in by the number of electrons in the outer shell of the atom. The bold type in Table 1.4 shows the unusual large increase in ionization energy. Na belongs to group I since only one electron is removed before the large increase. Similarly, Mg is in group II since two electrons are removed before the large increase.

	Na	Mg	Al	Si	P	S	Cl	Ar
1st	496	738	578	787	1012	1000	1251	1520
2nd	4562	1451	1817	1577	1903	2251	2297	2665
3rd	6912	7733	2745	3231	2912	3361	3822	3931
4th	9543	10540	11575	4356	4956	4564	5158	5770
5th	13353	13630	14830	16091	6273	7013	6542	7238
6th	16610	17995	18376	19784	22233	8495	9458	8781
7th	20114	21703	23293	23783	25397	27106	11020	11995
8th	25496	25661	27465	29287	29872	31719	33604	13842

Table 1.4: Successive ionization energies of period 3 elements (kJ/mol^{-1})

The successive ionization energies can also tell the number of electron shells in the atom. From the plot of successive ionization energies of sodium, the atom shows a large increase in energy between the first and second ionization energies. This suggests that the second electron is in a different energy level closer to the nucleus. There is also a significant difference between the ninth and tenth ionization energies which suggests that the tenth electron is also in a different energy level closer to the nucleus. The pattern shows that there are three shells with one electron in the outer, 8 electrons in the middle and 2 electrons in the inner.

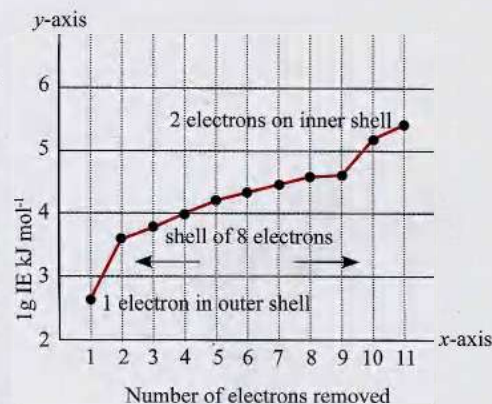


Fig. 1.10

Plot of successive ionization energies of Na

Fig. 1.10

Evidence for sub-energy levels

The first ionization energy of the elements in a period gives evidence for the presence of sub-levels. Figure 1.11 shows the first ionization energies for the elements of the period 2. Since the atomic radii decrease across the period, the general trend is an increase in the first ionization energy across the period. However, there are two irregularities in the pattern. The first ionization energy of boron is smaller than beryllium, and the first ionization



energy of oxygen is smaller than nitrogen.

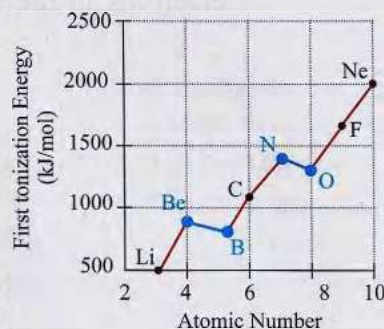


Fig. 1.11

These observations can be explained by the presence of sub energy levels. It requires less energy to remove the first electron from the 2p orbital in boron than it is to remove one from the filled 2s orbital in beryllium.

Be is $1s^2, 2s^2$

B is $1s^2, 2s^2, 2p^1$

In the case of nitrogen, the three electrons in the 2p orbitals all have the same spin, but in oxygen the fourth electron is paired in one of the 2p orbitals.

N is $1s^2, 2s^2, 2p^3$ $\uparrow \uparrow \uparrow$

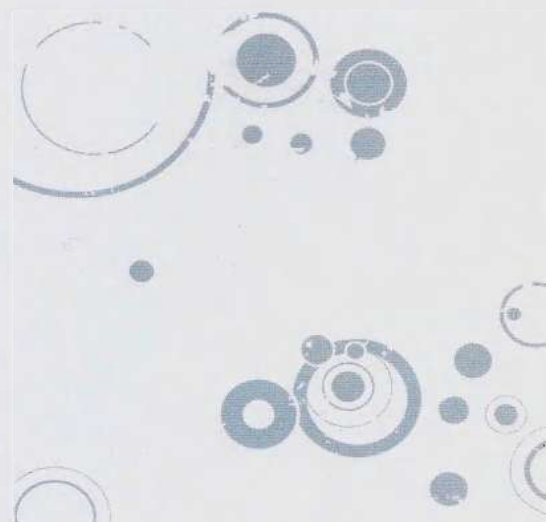
O is $1s^2, 2s^2, 2p^4$ $\uparrow\downarrow \uparrow \uparrow$

The electron-electron repulsion in the paired p orbital makes it easier to remove the paired electron with opposite spin, thus the first ionization energy of oxygen less than that of nitrogen.

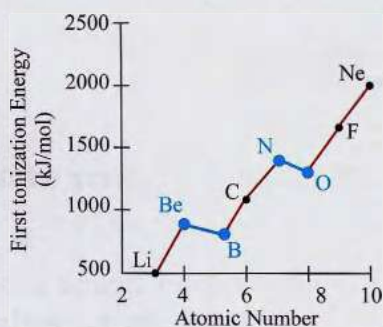


Questions

1. What do you understand by the following terms:
 - (a) mass number
 - (b) isotope
 - (c) relative atomic mass
2. The mass spectrum of lead shows the relative abundance of lead-204 is 1.4%, lead-206 is 24.1%, lead-207 is 22.1% and lead-208 is 52.4%. Calculate the relative atomic mass (A_r) of lead.
3. The analysis of a compound in the mass spectrometer involves *ionization*, *acceleration*, *deflection* and *detection*. Briefly explain how each of these processes is achieved in the mass spectrometer.
4.
 - (a) What are radioisotopes?
 - (b) Give two uses of radioisotopes.
 - (c) The mass spectrum of element X shows it has two isotopes of masses 63 and 65 with relative abundance of 75% and 25% respectively. Calculate the relative atomic mass of X.
 - (d) Write the electronic configuration of X given the atomic number is 29.
5. With the aid of suitable equations, show how the atomic mass and atomic number of an isotope change when a nucleus emits
 - (a) an alpha particle
 - (b) a beta particle
 - (c) gamma radiation



6. The graph below shows the trend in the 1st ionization energy from lithium to neon.



- (a) Explain why the 1st ionization energy of fluorine is greater than that of oxygen.
- (b) Why is the 1st ionization energy of oxygen less than that of nitrogen?
- (c) Explain how the data in the graph provide evidence for the existence of sub-shells within the atom.
7. The line emission spectrum of hydrogen consists of a series of lines in different parts of the electromagnetic spectrum.
- (a) Describe the processes that occur in the hydrogen atom that results in the formation of an emission spectrum.
- (b) Explain how the data from the emission spectrum provide evidence for discrete energy levels within the atom.
8. The electrons in an atom are accommodated in shells which are divided into sub-shells.
- (a) Construct a diagram to show the relative energies of all the sub-shells of principal quantum number 1, 2 and 3.
- (b) Draw diagrams to show the shapes of the orbitals of principal quantum number 2.
9. Write the electronic configuration in terms of s, p, d and f of the following species:
- (a) C
- (b) Na
- (c) Al^{3+}
- (d) S^{2-}
- (e) Ca^{2+}

10. (a) State three factors which influence the 1st ionization energy of an element.
- (b) The first eight ionization energies of an element X are as follows:

1 st	578
2 nd	1817
3 rd	2745
4 th	11575
5 th	14830
6 th	18376
7 th	23293
8 th	27465

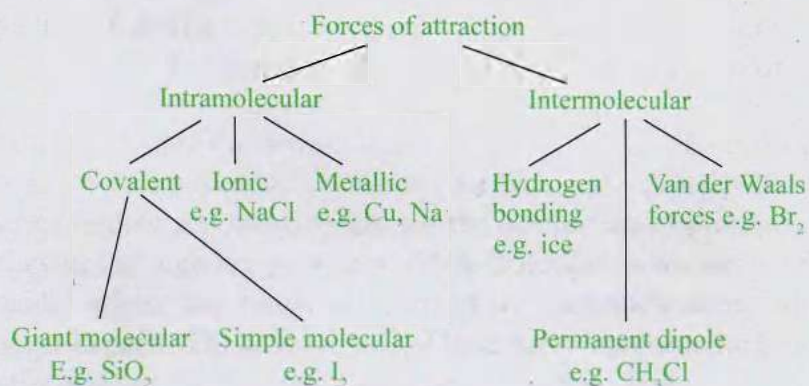
Suggest the group of the Periodic Table to which X is likely to belong. Give reasons for your answer.



Forces of attraction

The forces of attraction are the forces that exist within molecules or between molecules. These are described as intramolecular and intermolecular forces of attraction. Intramolecular forces are forces of attraction within molecules. These forces are strong and are as a result of chemical bonds. Intermolecular forces are forces of attraction between molecules and are weak forces. Fig. 2.1 below summarizes the forces of attraction.

Fig. 2.1
Forces of attraction



The physical state of matter depends on the strength of the forces of attraction in and between the particles. Solids have strong forces of attraction while liquids have moderate forces of attraction and gases have weak forces of attraction. Physical properties such as boiling point, melting point and solubility depend on the type of forces of attraction present in compounds.

Table 2.1
Physical properties of different types of compounds.

Bonding	Physical state	m.p./b.p.	Electrical conductivity	Solubility
Ionic	Solid	high	Conductor in molten or aqueous state	Soluble in polar solvent
Giant covalent (strong) (e.g. diamond)	Solid	high	Non-conductor (except graphite)	Insoluble
Simple molecular (weak Van der Waals forces)	Solid, liquid or gas	low	Non-conductor	Usually soluble in polar or non-polar solvent
Metallic	Solid (except Hg)	high	Good	Dissolve in other metals to form alloys

Melting involves breaking the lattice and overcoming the forces of attraction. The energy required to melt an ionic compound is high as it must overcome strong electrostatic forces of attraction in the lattice. For example, sodium chloride melts at approximately 800°C.

In simple covalent compounds, the molecules are held together by weak van der Waals forces and therefore the melting point is lower than ionic compounds. Metallic structures are held together by strong metallic bonds. The energy required to break the metallic lattice is relatively high when compared to ionic and covalently bonded compounds.

CHEMICAL BONDING

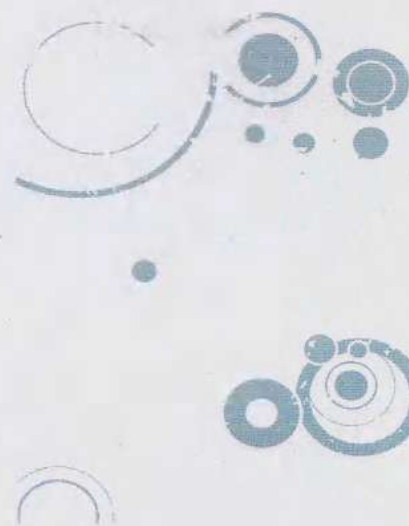
A bond is defined as a force of attraction that holds two or more atoms, ions or molecules together. This attraction is established between particles carrying positive and negative charges or between the positively charged nucleus and electrons.

In 1916, Kossel and Lewis observed that like the noble gases (except He), many elements were most stable when they contained eight electrons in their valence shell. They proposed that elements with less than eight valence electrons either gain, lose or share electrons to achieve a stable electronic configuration similar to that of the next higher or lower noble gas in the Periodic Table. As a result, chemical bonds were formed from the interaction of the electrons of one atom with the other. While some of their predictions have since been proven incorrect, for example many of the transition metal ions do not have an electronic structure like a noble gas, their work has established the basis of the theory of chemical bonding.



IONIC BONDING

Ionic bonding involves the transfer of electrons from a metal atom to a non-metal atom until the outer shells of the resulting ions are similar to those of a noble gas. The metals lose electrons and form cations, while the non-metals accept the electrons lost from the metals and form anions. The oppositely charged cations and anions are attracted to each other by what is called the **electrostatic force of attraction** which is a strong force that holds the ionic compound together. Ionic bonds are typically formed between metals with one, two or three electrons in their outer shells and non-metals with five, six or seven electrons in



their outer shells. The dot and cross diagrams below shows how ionic bonds are formed in sodium chloride, magnesium fluoride and lithium oxide.

Sodium chloride

In the formation of sodium chloride, each sodium atom donates its one outer shell electron to a chlorine atom forming Na^+ and Cl^- ions.

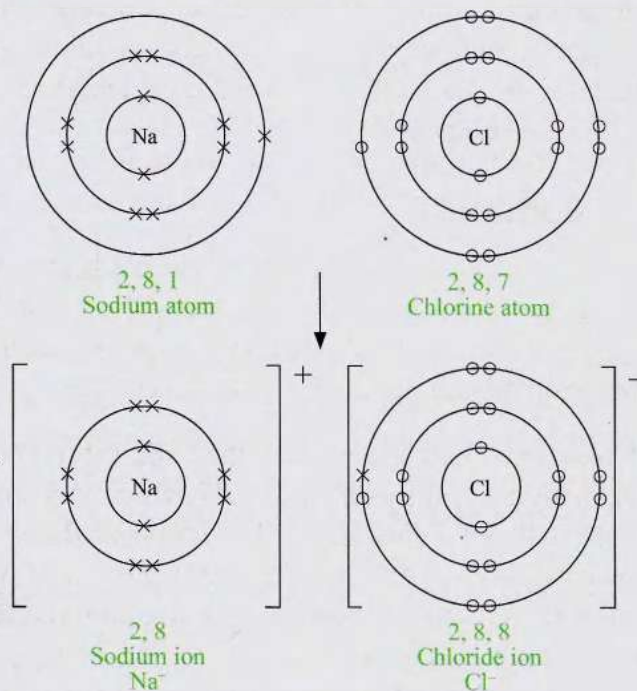


Fig. 2.2 Formation of sodium chloride

Magnesium fluoride

Magnesium atom loses its two outer shell electrons to form Mg^{2+} ion while each fluorine atom gains one electron to form F^- ions.

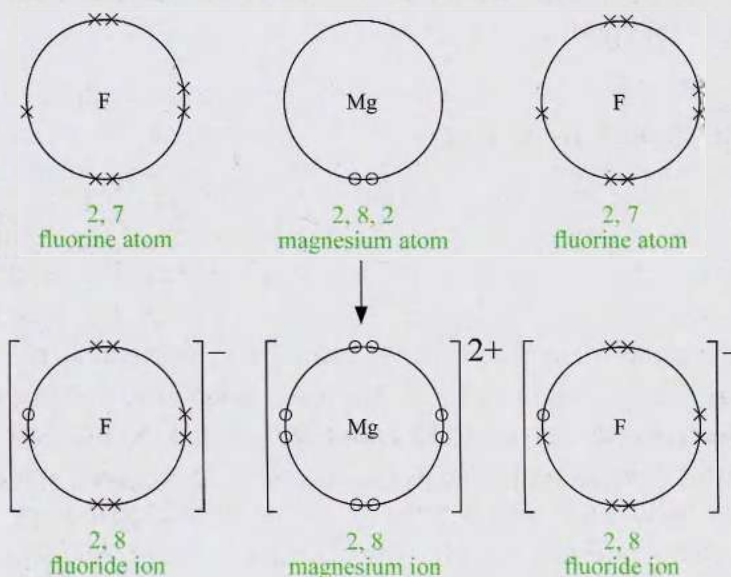


Fig. 2.3 Formation of magnesium fluoride

Lithium oxide

Each lithium atom loses its one outer shell electron to form Li^+ ions while oxygen gains two electrons to form O^{2-} ion.

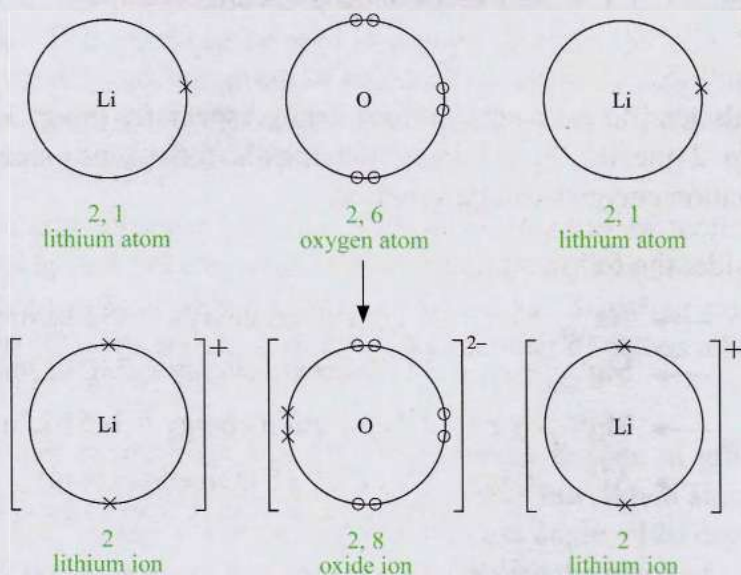


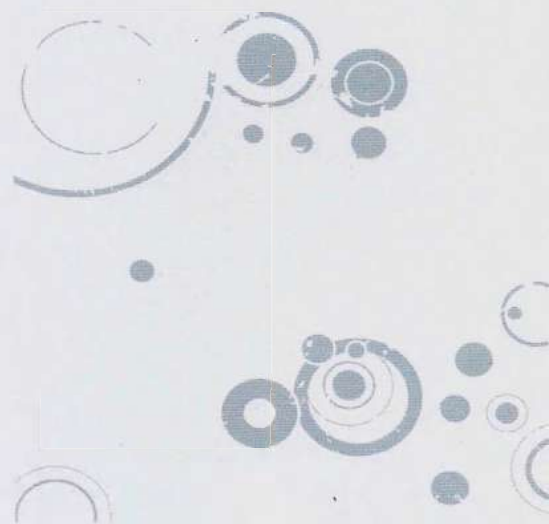
Fig. 2.4 Formation of lithium oxide

Properties of ionic compounds

- They are usually crystalline solids. Their regular arrangement of ions results in electrostatic attraction throughout the lattice imparting rigidity and strength to the structure.
- They have high melting points, boiling points, heats of fusion and heats of vaporization. A large amount of energy is required to break the solid structure that is held together by strong electrostatic attraction.
- They are hard and brittle. When a force is applied, the like charges repel each other which results in the crystal being shattered.
- They conduct electricity when molten or dissolved in water. The ions are free to move therefore mobile charge carriers are present to conduct electricity. They do not conduct electricity in the solid state because the ions have restricted motion and are not free to move.
- They are usually soluble in water. They have charges and will have solute-solvent interactions with polar water molecules.

Factors influencing formation of ionic compounds

Atoms gain or lose electrons to form ions. Thus the ionization energy and the electron affinity can be used as measurements of the ease with which ions are formed. In addition, there is also an

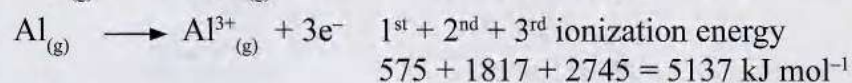
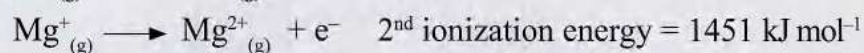
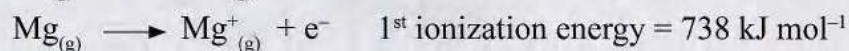
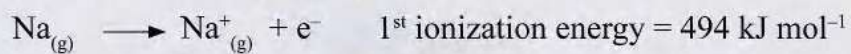


energy change when the separated ions are brought together to form the ionic compound. This is called the **lattice energy** which is the energy change when one mole of an ionic compound is formed from its gaseous ions under standard conditions.

Ionization energy

Metals tend to give up electrons easily especially group 1 and group 2 metals. In so doing the metals form ions once the ionization energies can be supplied.

Consider the following examples:



Sodium has the lowest ionization energy value and has a tendency to form ions faster than Mg or Al. It requires about four times the energy for $\text{Mg}_{(g)}$ to form $\text{Mg}_{(g)}^{2+}$ than for $\text{Na}_{(g)}$ to form $\text{Na}_{(g)}^{+}$. Also it takes about ten times the energy for $\text{Al}_{(g)}$ to form $\text{Al}_{(g)}^{3+}$ than for $\text{Na}_{(g)}$ to form $\text{Na}_{(g)}^{+}$. Generally smaller ionization energy values facilitate ion formation. Cations with single charges are formed more readily than cations with double charges while cations with triple charges are not formed as readily as cations with single or double charges.

Ionization energy values are affected by atomic radii, size of the nuclear charge and the screening effect of the inner electrons. If these factors influence the outer electrons such that the ionization energy values are too large, it will not be energetically feasible for ion formation to take place.

As the distance between the outer electron and the nucleus increases, the nuclear attraction for the outer electron decreases and the ionization energy decreases. Thus ions are formed more readily.

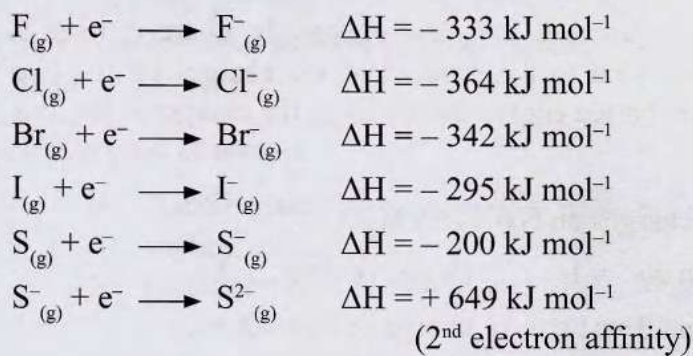
As atoms get larger, the screening effect of the inner electron becomes more effective and the outer electrons are loosely held to the nucleus. Thus the ionization energy decreases and ions are formed more readily.

For elements with the same number of shells, as the nuclear charge increases, the attraction of the nucleus for the outer electron

increases and the ionization energy increases. However, it must be noted that the atomic radii and electron screening can outweigh the effect of the nuclear charge. For example, in group 1 although Cs has a larger nuclear charge than Na, it loses an electron more readily than Na.

Electron affinity

In order for an anion to be formed, the non metal has to be able to accept electrons and become stable. When a non metal atom accepts an electron this is called its electron affinity. The 1st **electron affinity** is the enthalpy change when one mole of gaseous atoms is converted to gaseous ions with a single negative charge. Some electron affinity values are given below.



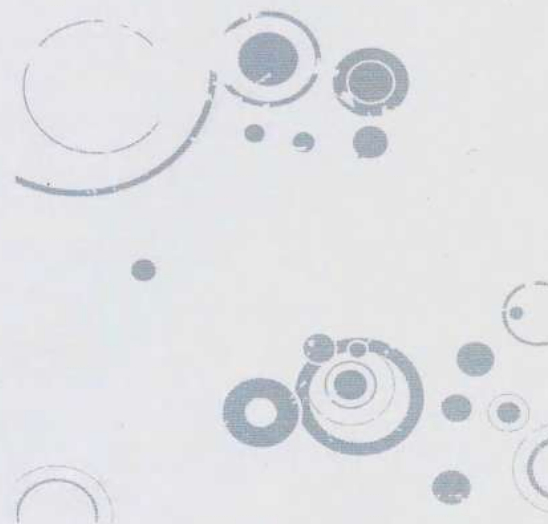
It should be noted that 1st electron affinity is the reverse of the 1st ionization energy. Generally the more exothermic the electron affinity, the more readily an anion is formed and the more stable it is. Chlorine has a more negative electron affinity value than iodine which implies that chlorine has a tendency to form the chloride anion faster than iodine form the iodide anion.

Electron affinities depend on the size of nuclear charge and the atomic radius. The smaller the atomic radius, the more effectively the nucleus attracts the incoming electron thus forming an anion more readily. The greater the nuclear charge for atoms of similar sizes, the more effectively the nucleus attracts the incoming electron thus forming an anion with greater ease.

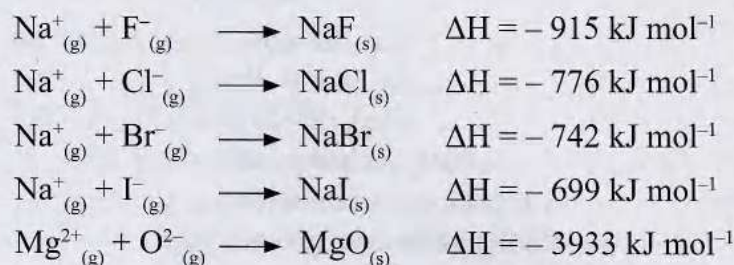
On moving across a period from left to right, the atomic radius becomes smaller and the nuclear charge increases. It is observed that the electron affinity values become more negative indicating that the incoming electron is held more firmly by the nucleus generating a progressively more stable anion.

Lattice energy

Lattice energy is a measure of the strength of the inter-ionic



attraction in ionic compounds. For a stable ionic compound to be formed from separate ions the overall energy change must be exothermic. Therefore all lattice energies are negative. The more exothermic the lattice energy, the more stable the ionic compound formed. The lattice energies for some ionic compounds are given below.



The force of attraction between oppositely charged ions is directly proportional to the product of the charges on the two ions. Therefore lattice energy increases as the charge of the ions increase.

Consider the charges on NaCl and MgO

charge on $\text{Na}^+ = 1$	charge on $\text{Mg}^{2+} = 2$
charge on $\text{Cl}^- = 1$	charge on $\text{O}^{2-} = 2$
ionic attraction = 1	ionic attraction = 4

Thus the lattice energy value of MgO (−3933) is much larger than that of NaCl (−776).

The force of attraction between oppositely charged ions is also inversely proportional to the square of the distance between the ions. This means that lattice energy is also dependant on the size of the cation and the anion. The smaller these are the more able they are to pack very tightly together in the lattice structure. Therefore the lattice energy increases as the size of the ion decreases.

Lattice energy $\propto \frac{1}{r_{\text{cation}} + r_{\text{anion}}}$ (where r is the radius)

Consider the size of the ions in NaCl, MgCl_2 and NaBr

	<i>NaCl</i>	<i>MgCl₂</i>	<i>NaBr</i>
Ionic radius	$\text{Na}^+ = 0.095 \text{ nm}$	$\text{Mg}^{2+} = 0.065 \text{ nm}$	$\text{Na}^+ = 0.095 \text{ nm}$
Ionic radius	$\text{Cl}^- = 0.181 \text{ nm}$	$\text{Cl}^- = 0.181 \text{ nm}$	$\text{Br}^- = 0.195 \text{ nm}$
Lattice energy $\propto$	$\frac{1}{0.095+0.181}$ = 3.62	$\frac{1}{0.065+0.181}$ = 5.59	$\frac{1}{0.095+0.195}$ = 3.45

This helps in explaining why the lattice energy of magnesium chloride (−2489 kJ mol^{−1}) is much higher than that of sodium

chloride (-776 kJ mol^{-1}) and sodium bromide (-742 kJ mol^{-1}).



COVALENT BONDING

Covalent bonds are formed when it is not energetically feasible for atoms to gain or lose electrons to form ions under normal conditions. These atoms share one or more pairs of electrons to gain a full outer shell. Each shared pair of electrons is considered a covalent bond. Each of the combining atoms contributes one electron to the bond. The attraction between the shared electrons and the nuclei of the combining atoms hold the atoms together.

Consider the formation of HCl.

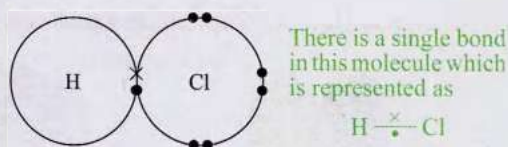


Fig. 2.5 Hydrogen chloride molecule

In this molecule, there is **one bonding pair** of electrons and three **non-bonding** or **lone pairs** of electrons on the chlorine atom.

In some cases, each atom donates two electrons to form two covalent bonds. This is called a double bond. Consider the oxygen molecule.

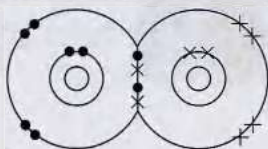


Fig. 2.6 Oxygen molecule

Similarly, a triple bond can be formed when each atom donates three electrons. For example, a triple bond is formed in the ethyne molecule.

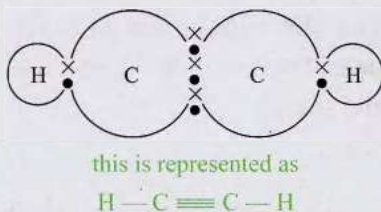


Fig. 2.7 Ethyne molecule

Another example is the triple bond in the N_2 molecule.

Molecular orbital

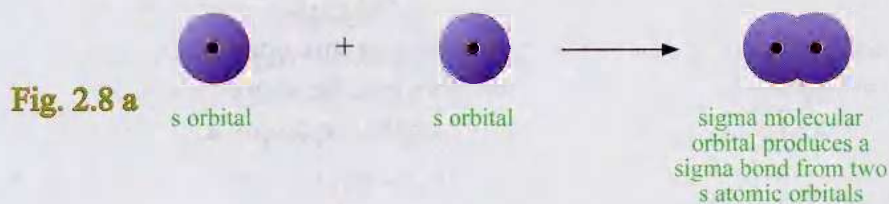
In covalent bonding, the atomic orbital of one atom overlaps and combines with the atomic orbital of another atom to form a bond. When atomic orbitals overlap and combine, molecular orbitals



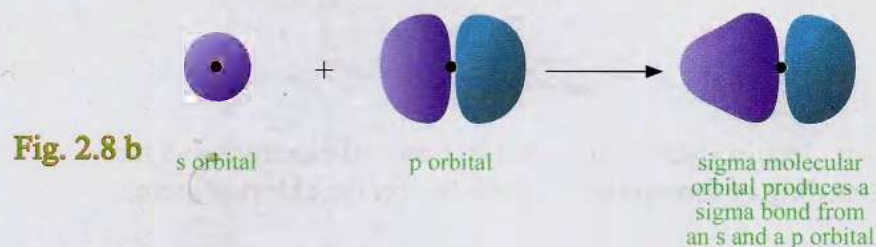
are formed. Molecular orbitals may be sigma molecular orbitals or pi molecular orbitals. Sigma molecular orbitals produce sigma bonds while pi molecular orbitals produce pi bonds.

Sigma bonds

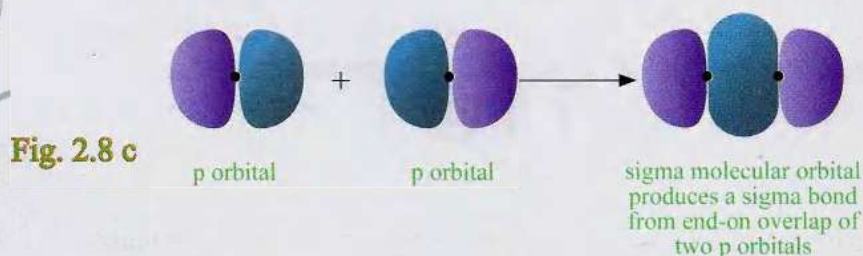
There are three possible ways for a sigma molecular orbital to form. The first possibility is the overlap of the two s orbitals.



The second possibility is the overlap of an s and a p orbital.



The third possibility is the end-on overlap of two p orbitals.



In a sigma bond, orbital overlap is always along the axis of the nuclei so that the bond is centered directly between the two nuclei. A sigma bond gives the maximum possible electron density between the two nuclei therefore it is a strong bond. Compounds with sigma bonds are stable.

Pi bonds

A pi molecular orbital is formed by sideways overlap of two parallel p orbitals that are perpendicular to a sigma bond. The electron density of the pi bond is distributed above and below the plane of the sigma bond. The electron density is zero along the axis of the nuclei. A pi bond is weaker than a sigma bond hence compounds with pi bonds are reactive.

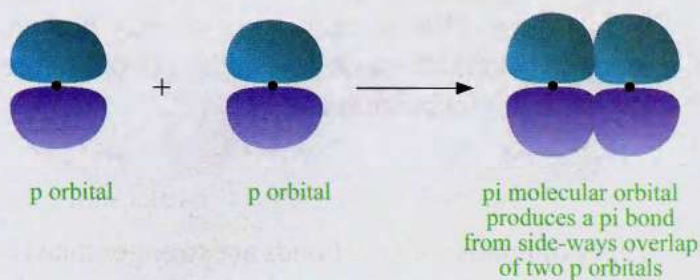


Fig. 2.9

Bond strength, bond length and bond enthalpy

The strength of a covalent bond depends on the effectiveness of the overlap between the atomic orbitals. If the overlap is large the bond is very strong whereas a small overlap implies that the bond is relatively weak.

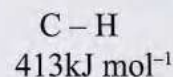
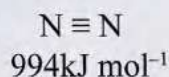
The *bond length* is the distance between the nuclei of two atoms that are bonded to each other. Generally shorter bond lengths give rise to stronger bonds. If the bond length is short then the nuclei will hold on to the electrons in the covalent bond very strongly. This implies that there is a very effective overlap between atomic orbitals. Half the bond length of a single bond between two similar atoms is called the *covalent radius*. The *bond order* is the number of electron pairs shared between two atoms in the formation of a covalent bond. In the alkanes the bond order between the carbon atoms is one since a single bond is present. In the alkenes the bond order is two whereas in the alkynes and in nitrogen the bond order is three.

The molar *bond energy or enthalpy* of a bond between two atoms is the energy required to break 1 mole of the bonds between the atoms. Bond energy values are a direct measure of the strength of a bond. The higher the bond energy, the stronger the bond and the more stable is the compound. Factors affecting bond energy are:

- Bond length – shorter bond length, stronger bond and larger bond energy e.g. the bond energy of H – H is +436 kJ mol⁻¹ while that of F – F is +158 kJ mol⁻¹.
- Number of bonds (single, double or triple bonds) – the triple bond in nitrogen is strong compare to the single bond of C – H. Nitrogen molecules are described as being relatively inert in nature and undergo very few reactions. This inertness results from the shortness and strength of the triple covalent bond present in the molecule. Short bond lengths imply that the covalent bond in the molecule is very strong and a lot of energy is required to break it apart. The bond energy of N₂



is very large (994 kJ mol^{-1}) that is only broken under extreme conditions such as in lightning discharges or in the internal combustion engine.



- Types of bonds – sigma bonds are stronger than pi bonds therefore the bond energy is higher for a sigma bond.
- Bond polarity – higher the polarity, stronger the bond and larger the bond energy e.g. bond energy of $\text{H} - \text{F}$ is $+568 \text{ kJ mol}^{-1}$ while that of $\text{H} - \text{Cl}$ is $+432 \text{ kJ mol}^{-1}$.

Bond energy values can be used to

- compare the strengths of bonds
- understand structure and bonding
- estimate the enthalpy changes in reactions
- understand the mechanisms of chemical reactions

Table 2.2

Bond length and bond energy of the hydrogen halides.

Bond	Bond length	Bond energy
$\text{F} - \text{H}$	0.092 nm	568 kJ mol^{-1} (Strongest bond)
$\text{Cl} - \text{H}$	0.127 nm	432 kJ mol^{-1}
$\text{Br} - \text{H}$	0.141 nm	366 kJ mol^{-1}
$\text{I} - \text{H}$	0.161 nm	296 kJ mol^{-1} (Weakest bond)

Bond polarity

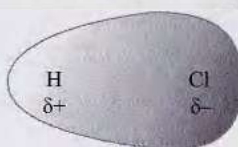
In a covalent bond, the electron density can be symmetrically distributed between the two atoms constituting the covalent bond or they can be unsymmetrically distributed. Distribution of electron density is dependent on the electronegativity of the elements involved. **Electronegativity** measures the ability of an atom to attract an electron in a covalent bond. A covalent bond formed between atoms which differ in electronegativity is called **a polar covalent bond**. The bonding electron density is greater in the region of the more electronegative atom. This uneven sharing of the electron density results in the bond being slightly positive at the less electronegative end and slightly negative at the more electronegative end. See Fig. 2.10

Nonpolar covalent bond



Symmetrical distribution of electron density

Polar covalent bond



Unsymmetrical distribution of electron density

Cl is more electronegative than H and pulls the electrons of the covalent bond towards itself. As such, the H end develops a small positive charge called a δ^+ charge and the Cl end develops a small negative charge called a δ^- charge.

Fig. 2.10

A molecule such as HCl is described as a polar molecule because it contains partial charges. The bond strength increases in a polarized covalent bond due to the electrostatic attraction between the slightly positive and slightly negative terminals.

Table 2.3

Electronegative values of some elements

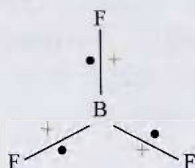
Elements	Electronegativity values
F	4
O	3.5
Cl	3
N	3
Br	2.8
I	2.5
C	2.5
H	2.1



CO-ORDINATE OR DATIVE COVALENT BONDING

In normal covalent bonding each atom donates one electron to the covalent bond. However in some cases it is possible for one atom to donate both electrons to create the covalent bond. When a covalent bond is formed by the donation of both electrons from one atom, a dative or co-ordinate covalent bond is formed. In order for a dative bond to form an atom must be present with at least one lone pair of electrons that can be donated easily and there must be another atom with available space in its orbital to accommodate the electron pair. Consider the following molecules:

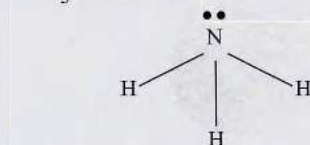
BF_3 Molecule



Boron only has 6 electrons in its outer electron shell and can accommodate two additional electrons to complete its octet.

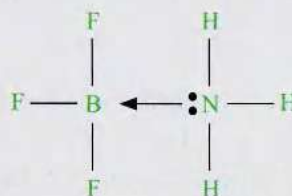


NH₃ Molecule

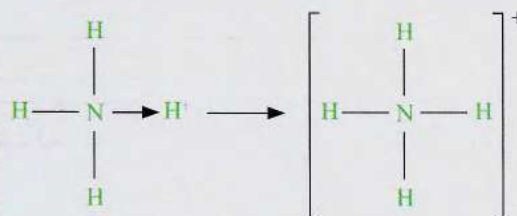


Nitrogen has a lone pair of electrons which can be donated easily.

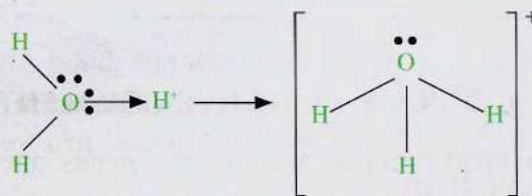
When BF₃ and NH₃ combine, a new compound with the formula BF₃·NH₃ is produced. Here the nitrogen atom donates its lone pair of electrons to the B atom completing its octet.



Similarly, when ammonia acts as a base by accepting a proton, it uses its lone pair to form a covalent bond with H⁺.



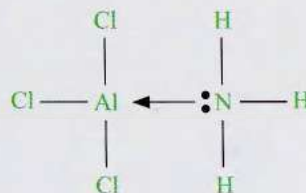
When water forms the hydroxonium cation, the oxygen uses its lone pairs to form a dative bond with H⁺.



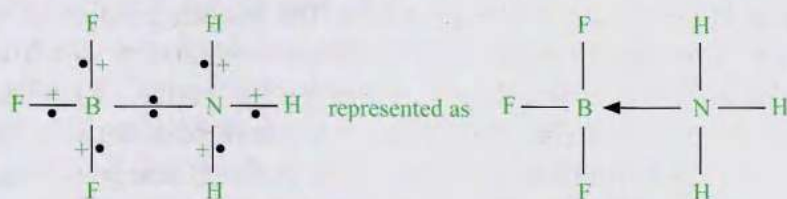
In carbon monoxide, there is a dative bond between the carbon atom and oxygen atom in which oxygen donates a lone pair of electrons to carbon.



When AlCl₃ and NH₃ combine, a compound with the formula AlCl₃·NH₃ is formed.



The dative bond formed here is indistinguishable from a normal covalent bond and can only be distinguished when the electron distributions are worked out. An arrow is usually used to show which atom is donating the electron pair.



When gaseous molecules of AlCl_3 are cooled, the molecules end up having the formula Al_2Cl_6 . Aluminium chloride exists as a dimer i.e. a molecule made by combining two similar smaller molecules. This **dimerization** process as it is called, results from the formation of dative bonds.

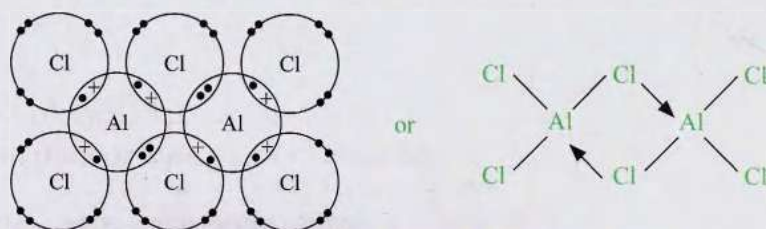
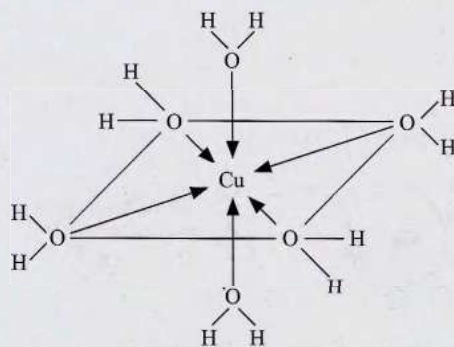
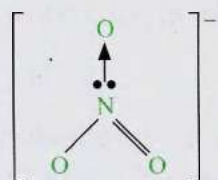


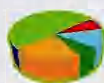
Fig. 2.11
Dimerization
of aluminum
chloride

In transition metal chemistry molecules called ligands which have lone pairs of electrons are donated into the d-orbitals of the transition metal forming complexes such as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. In this complex, water donates lone pairs of electrons into the available d-orbitals of copper.



Another example is the nitrate (V) ion NO_3^-



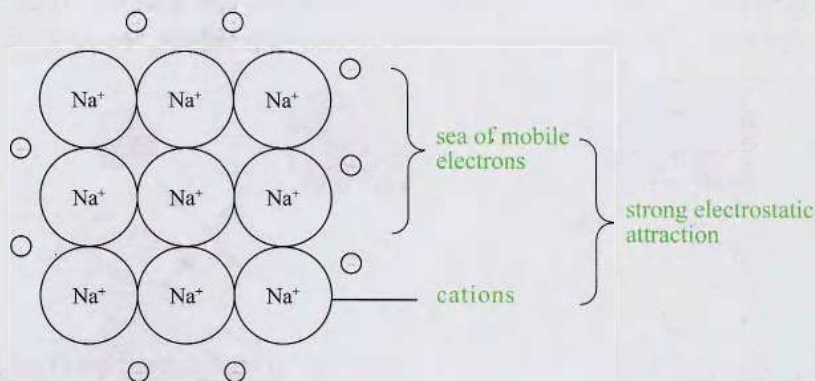


METALLIC BONDING

In metallic bonding, the metal atoms come together and donate their valence electrons to form a “sea” of mobile electrons which is communally shared among the resulting cations. The cations organize themselves in a lattice structure in which the sea of electrons is free to move through the lattice. Repulsion between cations exists, but the overall attraction between the mobile electrons creates a large electrostatic attraction which is extremely stable. Consider the formation of metallic sodium, if nine sodium atoms come together, there will be nine electrons that are donated to the sea of electrons.

Fig. 2.12 a

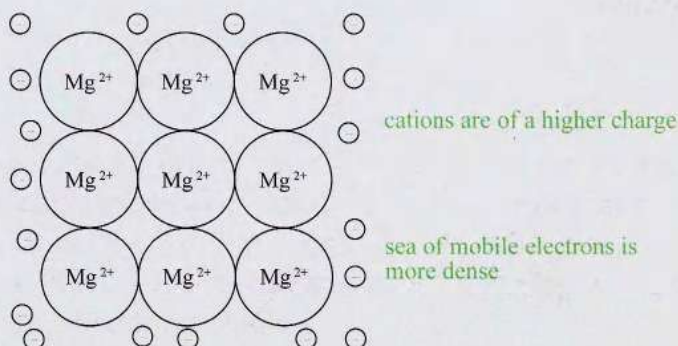
Metallic bonding
in sodium



Consider the formation of metallic magnesium, when nine atoms combine, there will be eighteen electrons donated to the sea of electrons.

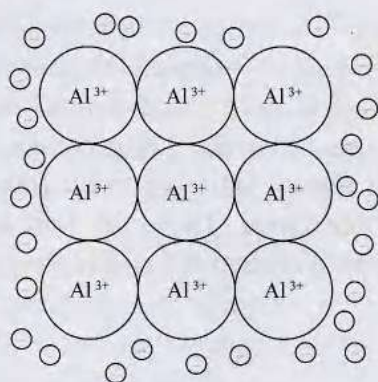
Fig. 2.12 b

Metallic bonding
in magnesium



Consider the joining of nine aluminium atoms, there will be twenty seven electrons donated to the sea.





cations are very highly charged
sea of mobile electrons is most dense

Fig. 2.12c

Metallic bonding in aluminium

Generally the more electrons donated towards the sea of electrons, the stronger the metallic bond. Also the smaller the cations, the more tightly they are packed in the lattice of cations so increasing the strength of the metallic bonds. Aluminium is therefore expected to have a higher melting point and is stronger than magnesium.

Properties of metals

- Usually high density solids with high melting and boiling points.
- Good conductors of heat and of electricity. The mobile electrons act as mobile charge carriers which make metals good conductors.
- Shiny, usually reflecting light of all wavelengths.
- Malleable and ductile. When stress is applied the cations can slide over each other and as such metals can be beaten into shapes and drawn into wires.

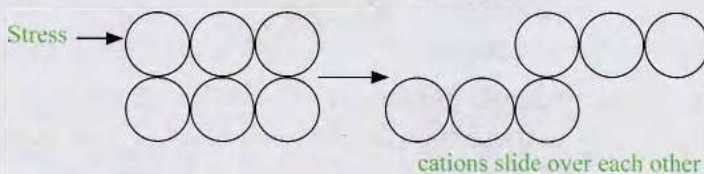
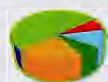


Fig. 2.13



INTERMOLECULAR FORCES OF ATTRACTION

Intermolecular forces of attraction can be defined as the attractive forces between molecules. They are generally very weak, too weak to be called bonds (in relation to intramolecular forces such as, ionic, covalent and metallic bonding). However, if these forces did not exist, gases would not be able to condense to liquids, nor would liquids be able to freeze to form solids. When the two aforementioned processes occur, heat energy is given out as molecules attract one another and bonds are formed. Conversely, heat energy has to be supplied to melt a solid or vaporize a liquid



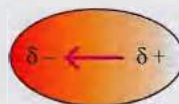
because energy is needed to overcome the attractive forces holding the molecules together. Thus intermolecular forces are responsible for compounds existing as solids, liquids and gases. All molecules experience intermolecular attractions however the attraction is weaker in some molecules than in others. Intermolecular forces of attraction are classified into three types. These are van der Waals forces, permanent dipole-dipole attractions and hydrogen bonding.

Van der Waals Forces

Van der Waals forces are the weakest of all the intermolecular forces. These exist between non-polar atoms or molecules. They generally result from the shifting distributions of the electron cloud within the atom or molecule. These interactions were first documented by J. D. van der Waals, a Dutch physicist and chemist. Originally van der Waals forces referred to all intermolecular interactions however it is now specifically referred to as **induced dipole-induced dipole** attractions in many texts.

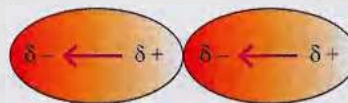
On average the electron cloud of a non-polar atom or molecule is evenly distributed. However since the electron cloud is in a state of continual motion, at a given point in time, the electron cloud may be more concentrated on one side of the atom or molecule more than the other. This gives the atom or molecule a temporary dipole moment i.e. opposite charges separated by a small distance.

Fig. 2.14 a



The resulting dipole induces dipoles in the neighbouring atoms or molecules and these then attract each other. These attractions are called induced dipole-induced dipole attractions or instantaneous dipole attractions. Examples of atoms and molecules with van der Waals forces of attraction are liquid noble gases or Br_2 liquid respectively.

Fig. 2.14 b



As the electron cloud continues to move, the direction of polarity in the atoms and molecules change but the intermolecular forces of attraction remain. The overall electron density remains evenly distributed within each atom or molecule as no permanent dipole exists.

As the number of electrons increases in a system, the size of the temporary partial charges also increases. This results in stronger attraction between atoms or molecules and leads to the conversion of gases into liquids and liquids to solids (change of state). This trend can be seen in group VII of the Periodic Table. As we descend the group of halogens, there is a change of state from gas to solid (Cl_2 is a gas, Br_2 is a liquid and I_2 is a solid) due to stronger van der Waals forces.

Similarly, stronger van der Waals forces lead to an increase in melting and boiling points down group VIII, the noble gases. Helium, which only has two electrons, has a boiling point of -269°C while Radon with an atomic number of 86 has a boiling point of -62°C .

Another example of van der Waals forces is seen in graphite, one of the allotropes of carbon. In graphite, the carbon atoms are bonded to three other carbon atoms (bond angle $=120^\circ$). As a result, one p-orbital is above and below the plane of a layer. This p orbital is unaffected by bonding and contains one electron. The p orbitals overlap forming a delocalized electron cloud. As a result van der Waals forces loosely hold the layers in graphite together. The distance between layers is 0.335 nm as opposed to the bond length of 0.142 nm within a layer (longer bond are weaker).

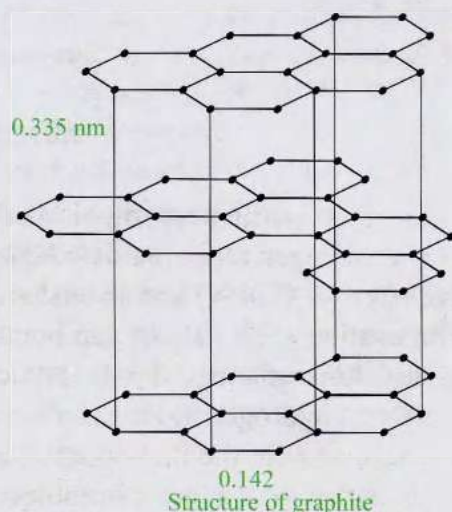


Fig. 2.15

The van der Waals forces between layers of graphite are responsible for its soft and slippery property. It is therefore an effective lubricant e.g. in WD-40. Graphite is also an electrical conductor due to the presence of mobile charge carriers between the layers e.g. dry cell batteries made from graphite.



Permanent dipole-permanent dipole attractions

Permanent dipole-permanent dipole attractions exist between polar molecules. These are molecules in which atoms in the covalent bond differ in electronegativity. The bonding electron density is greater in the region of the more electronegative atom. This uneven sharing of the electron density results in charge dispersion in the molecule which gives rise to a permanent dipole. HCl molecule is an example of a polar molecule with a permanent dipole.



Fig. 2.16 a

a polar covalent molecule, uneven distribution of electron density results in a permanent dipole

The neighbouring molecules are attracted to each other forming permanent dipole-permanent dipole attractions. Permanent dipole-permanent dipole attractions are stronger than induced dipole-induced dipole attractions.

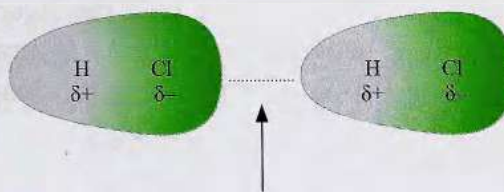


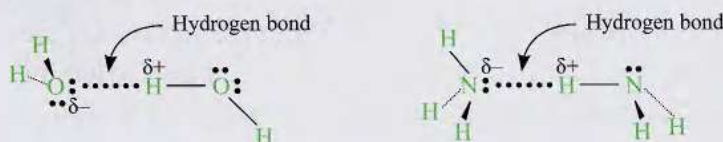
Fig. 2.16 b

permanent dipole-permanent dipole attraction between molecule

Hydrogen bonding

A hydrogen bond is a permanent dipole-permanent dipole attraction between a hydrogen atom that is covalently bonded to an electronegative atom (F, O or N) and an unshared electron pair on another electronegative atom. Hydrogen bonding is different from permanent dipole-permanent dipole attractions in other polar molecules in that a hydrogen atom has no inner electrons to set up forces of repulsion with the non-bonding electrons of the other atom. This gives rise to stronger intermolecular forces.

The two examples below show hydrogen bonding in water molecules and in ammonia molecules.



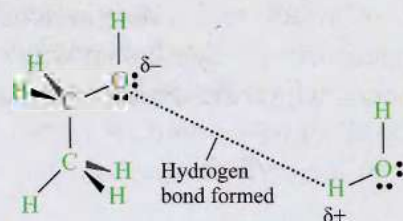
Hydrogen bonds are stronger intermolecular forces of attraction than ordinary permanent dipole-permanent dipole attraction. These bonds are directional and are shown as a dotted line to indicate that they are weaker than a covalent bond. There is a proton being shared between the two electronegative atoms, the proton is said to be in a dynamic state ('flickering between atoms').

Hydrogen bonding has a significant effect on the boiling points of compounds in which it exists. Substances with hydrogen bonds have unusually high boiling points due to the extra energy that must be used to separate these strong intermolecular forces between the molecules. For example NH_3 , H_2O and HF have much higher boiling points than expected. If we compare, the boiling point of H_2O (100°C) to that of a molecule of similar molecular mass which does not undergo hydrogen bonding such as CH_4 (-164°C), water has a much higher boiling point.

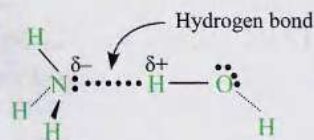
Each water molecule can form four hydrogen bonds with surrounding water molecules. This is because each water molecule has two lone pairs and two polar hydrogens. The ratio of lone pairs to polar hydrogens is ideal for all of the lone pairs and polar hydrogens to form hydrogen bonds.

In the case of ammonia, each ammonia molecule has one lone pair and three polar hydrogens. The ratio of lone pairs to polar hydrogens limits the amount of hydrogen bonds that can be formed. This means that each ammonia molecule can form only two hydrogen bonds with surrounding ammonia molecules. One hydrogen bond can be formed with the lone pair and one can be formed with only one of the polar hydrogens. This accounts for why water has a higher boiling point than ammonia.

The presence of hydrogen bonds also affects the solubility of compounds in polar solvents e.g. $\text{C}_2\text{H}_5\text{OH}$ in H_2O . Both the ethanol and the water are molecular substances with O-H bonds. Ethanol dissolves in water because hydrogen bonds are formed between the ethanol and water molecules when they are mixed.



Another example is ammonia dissolving in water. The H on a water molecule is attracted to an N of an ammonia molecule to form a hydrogen bond.



Importance of hydrogen bonding in water and ice

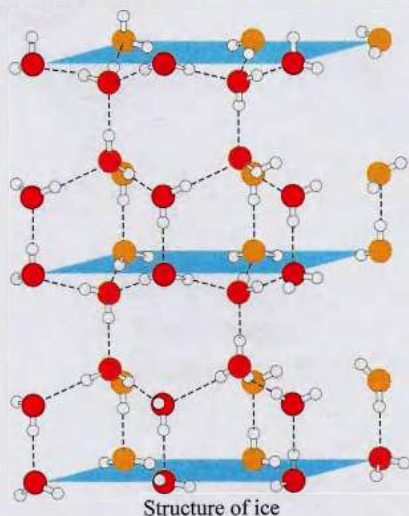
Hydrogen bonding gives rise to the unexpectedly high values for the melting point of ice and the boiling point of water. If water behaved as a normal polar molecule it would have a boiling point of about -100°C . However water boils at 100°C which is abnormal. The main reason for this abnormal behaviour results from the strong hydrogen bonds between water molecules. Therefore it takes a lot more energy to break the hydrogen bonds to free the water molecules as the gas. Without these hydrogen bonds, water would probably exist as a gas at normal atmospheric conditions. This means that oceans, lakes and rivers might not exist without hydrogen bonds between water molecules.



Water strider walks on the surface of water

Hydrogen bonds also cause water to have a high surface tension and a high viscosity. Due to the high surface tension of water, small objects such as razor blades will float on the surface of water. Similarly, small insects such as water striders and pond skaters can walk on the surface of water. High surface tension of water is also significant to plants. It allows water to rise through the xylem vessels in root and stems by capillary action.

Picture



Another influence of hydrogen bonding in water is its high specific heat capacity (ten times that of rock). This means that large amounts of heat energy are needed to evaporate small amounts of water. Therefore the oceans are slow to warm up during the summer months and cool during winter. Since water can absorb a lot of heat with only a small increase in temperature, it aids in maintaining the surface temperature of the Earth.

The arrangement of water molecules in ice creates an open structure which makes ice less dense than water. This is different from most compounds which are denser in the solid state than in the liquid state.

Fig. 2.18

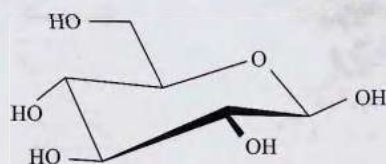


When ice melts, the open lattice breaks down and molecules can get closer to each other until water reaches its maximum density at 4°C. This means that ice floats on water and water freezes from the surface downwards. This anomaly is significant in nature. When lakes freeze during winter, ice floats on the surface of the water and insulates the rest of the lake from freezing. The densest water at 4°C sinks to the bottom of the lake. Thus the majority of the water in the lake or pond stays in the liquid state and the creatures that inhabit the lake can survive. If water behaved like an ordinary liquid, the lake would freeze from the bottom up thus killing aquatic organisms.

Another consequence of the abnormal expansion of water occurs when water freezes in pipes and car engines. The resulting expansions can rupture the metal, the leak only becoming apparent when the ice melts. A similar example is seen in the weathering or erosion of rock. Water seeps into cracks in the rock, freezes and expands. The resulting force splits the rock, leading to rock fall and slides.

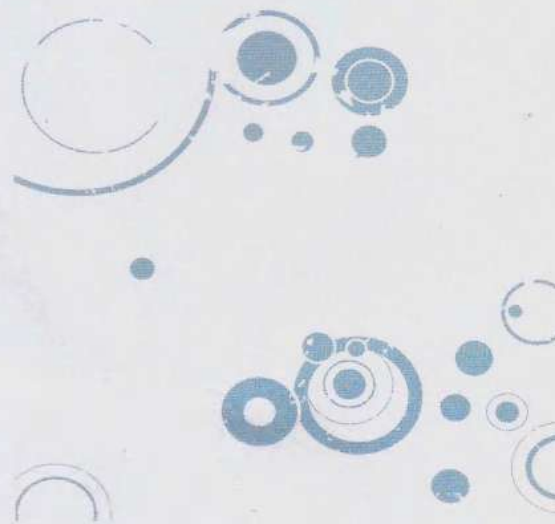
Hydrogen bonding in plants and animals

Sugars such as glucose contain several polar OH groups which give rise to a large number of hydrogen bonds. As such glucose is very soluble in water.

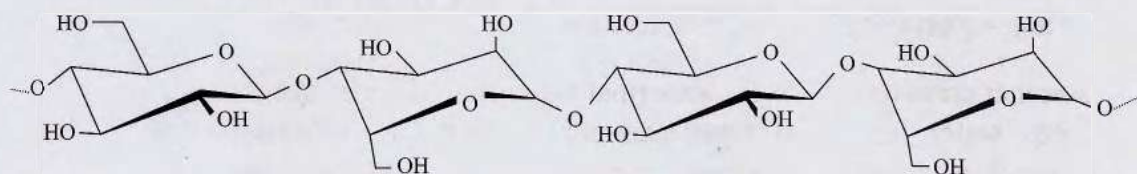


Ring structure of glucose

Glucose is a ready source of energy. Its carbon atoms are easily oxidized to form carbon dioxide, releasing energy in the process. However, unlike other hydrocarbon fuels which are insoluble in water, the numerous OH groups in glucose allow it to readily form hydrogen bond with water molecules making it highly soluble in water. This allows the glucose to be transported easily within biological systems, for example in the bloodstream of animals or the sap of plants. The average adult has 5-6 grams of glucose in the blood which supplies the energy needs of the body for about 15 minutes. Thereafter the glucose level must be replenished from compounds stored in the liver. Because glucose is found in ripe fruits, the nectar of flowers, leaves, sap and blood, over the years it has been given various common names, such as starch sugar, blood sugar, grape sugar and corn sugar.



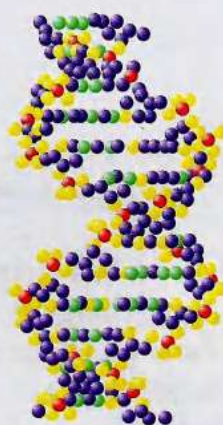
Cellulose is formed by large numbers of glucose molecules joined by covalent bonds. Since wood is largely cellulose, hydrogen bonds are responsible for holding the chains of cellulose together in wood. Thus it is easier to split wood along its length where hydrogen bonds hold the cellulose chains together rather than across where covalent bonds hold the glucose units together. Cellulose is used to make paper. Untreated paper becomes soft and tears very easily when wet because the cellulose strands form hydrogen bonds with the water molecules more readily than they do with each other.



structure of cellulose

Proteins contain the amide linkage. These linkages form hydrogen bonds with each other. The bonds are split very easily with high temperatures and this account for the denaturing of proteins and enzymes at high temperatures. DNA molecule looks like a spiral ladder where the rungs are formed by base molecules, which occur in pairs. These sequences of base pairs represent the genetic information. The two parallel chains of nucleic acids in DNA are held together by hydrogen bonds between specific pairs of bases.

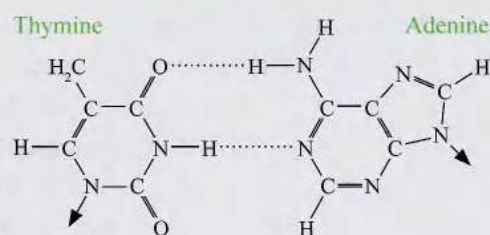
Fig. 2.19



DNA model



DNA double helix



hydrogen bond between bases

We have seen numerous examples of the importance of the intermolecular forces of attraction ranging from effects on the climate to continuation of life, these forces play a vital role in many aspects of nature and our everyday lives.



THE VALENCY SHELL ELECTRON PAIR REPULSION THEORY

The valence shell electron pair repulsion theory predicts the shapes and bond angles of simple covalent molecules. This theory suggests that the electron pairs around an atom repel each other and arrange themselves in space so as to minimize the repulsive forces.

The shapes of molecules are determined primarily by the number of bonding pairs and lone pairs of electrons around a particular atom called the central atom. The interactions between these bonding pairs are such that an electron pair in one bond repels those of another bond. This interaction is called **bonding pair-bonding pair repulsion**. Similarly repulsion between lone pairs and bonding pairs is called **lone pair-bonding pair repulsion**. Also repulsion between lone pairs is called **lone pair-lone pair repulsion**.

The strength of the repulsion between electron pairs depends on the proximity of each pair to the central atom. Lone pairs are closer to the central atom than bond pairs since the lone pairs have no other nearby positive nucleus to pull them away from the central atom. Bond pairs are attracted by a second nucleus and so they are drawn further away from the central atom. The repulsion between electron pairs is inversely proportional to the distance between them. **Thus lone pair-lone pair repulsion is stronger than lone pair-bond pair repulsion which in turn is stronger than bond pair-bond pair repulsion.**

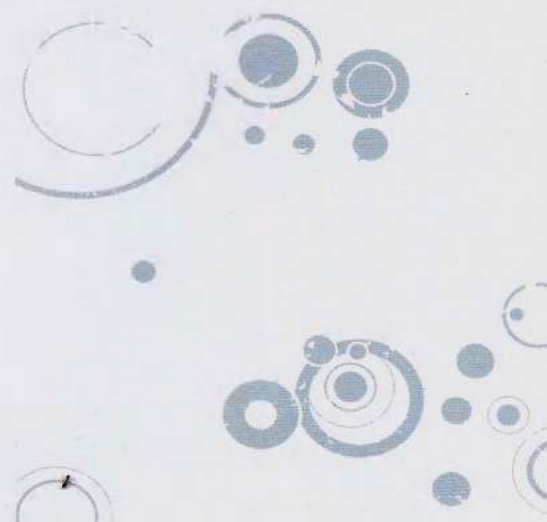
Lone pair-lone pair > lone pair-bond pair > bond pair-bond pair

The presence of a lone pair in a molecule tends to push the other bond pairs closer together. This will result in smaller bond angles in molecule containing a lone pair.

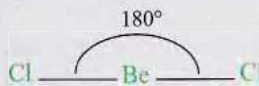
Molecules may have different shapes depending on the number of lone pairs and bond pairs surrounding the central atom.

Linear molecules

These have **two bond pairs** which arrange themselves the maximum distance apart to minimize repulsion. The bond angle will therefore be 180° and adopt a linear configuration. Examples include BeCl_2 and CO_2 .



Beryllium chloride



Carbon dioxide

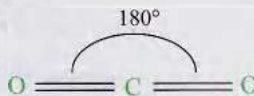


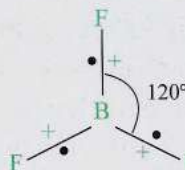
Fig. 2.20

In carbon dioxide, a double bond acts as a single pair of shared electrons. Similarly in a triple bond like ethyne, the electrons act as a single pair of shared electrons.

Trigonal planar molecules

These have **three bond pairs** around a central atom which arrange themselves at maximum distance apart to minimize repulsion. A trigonal planar molecule is therefore produced with a bond angle of 120°. Examples include BF₃, SO₃ and the H₂C=CH₂ as in ethene.

Boron trifluoride



Ethene

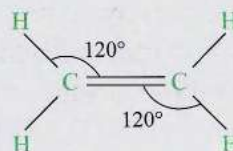


Fig. 2.21

Tetrahedral molecules

These have **four bond pairs** around a central atom which arrange themselves at maximum distance apart to form a tetrahedral shape with bond angles of 109.5°. Examples include CH₄, CHCl₃ and POCl₃.

Fig. 2.22

Methane



Trigonal bipyramidal molecules

These have **five bond pairs** around a central atom. The bond pairs arrange themselves to form a trigonal bipyramidal shape. Three atoms form the trigonal plane with bond angles of 120° while two atoms form the pyramid which is perpendicular to the trigonal plane. Examples include PF_5 and PCl_5 .

Phosphorous pentafluoride

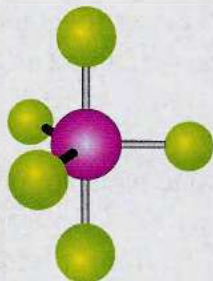
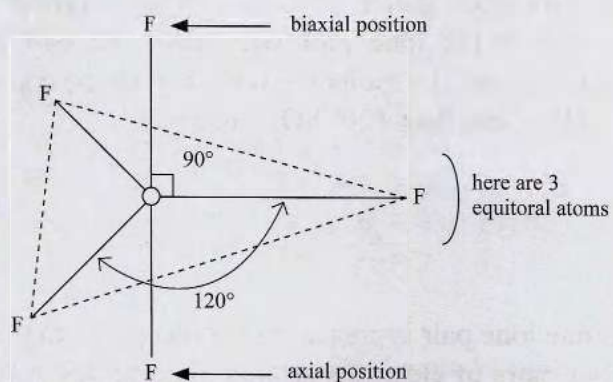


Fig. 2.23

Octahedral molecules

These have **six bond pairs** around a central atom. The bond pairs arrange themselves to form an octahedral shape with bond angles of 90° , e.g. SF_6 .

Sulphur hexafluoride

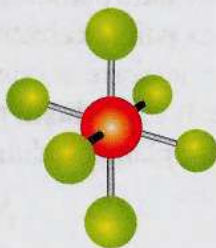
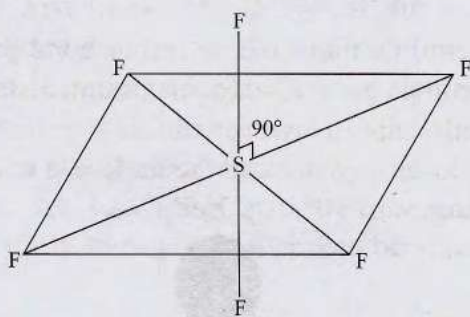


Fig. 2.24

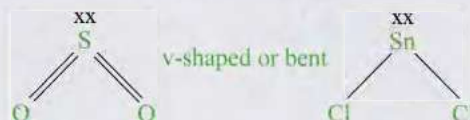


Effect of lone pairs on the shapes of molecules

The presence of lone pairs influences the shapes of molecules. The number of bond pairs and lone pairs are used to predict a suitable structure for a molecule. Remember that the lone pairs repel the bond pairs more strongly.

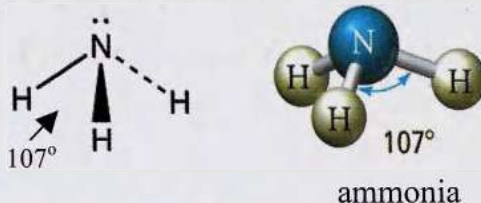
One lone pair - If one lone pair is present in a molecule with two bond pairs, the three pairs of electrons arrange themselves at maximum distance apart to form trigonal planar molecule. However the lone pair will repel the two bond pairs closer together and the molecule will be V-shape e.g. with a bond angle slightly less than 120° SO_2 and SnCl_2 .

Fig. 2.25 a



If one lone pair is present in a molecule with three bond pairs, the four pairs of electrons arrange themselves at maximum distance apart to form a tetrahedral shape. However the lone pair will repel the three bond pairs closer together and the molecule adopt a trigonal pyramidal shape with bond angles less than 109.5° . For example, NH_3 has a bond angle of 107° .

Fig. 2.25 b



Two lone pairs - If two lone pairs are present in a molecule with two bond pairs, the four pairs of electrons arrange themselves at maximum distance apart to form a tetrahedral shape. However the lone pairs will repel the two bond pairs closer together and the molecule will be V-shape with bond angle less than 109.5° . For example, H_2O has a bond angle of 105° .

Fig. 2.26 a



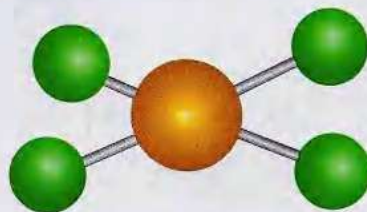
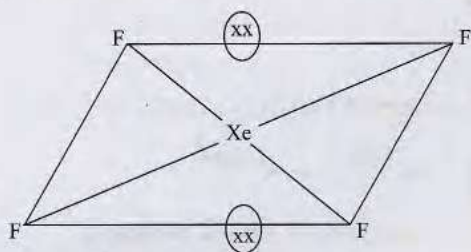


Fig. 2.26 b

Shapes of cations and anions

Cations and anions also assume particular geometry that can be predicted by the VSEPR theory.

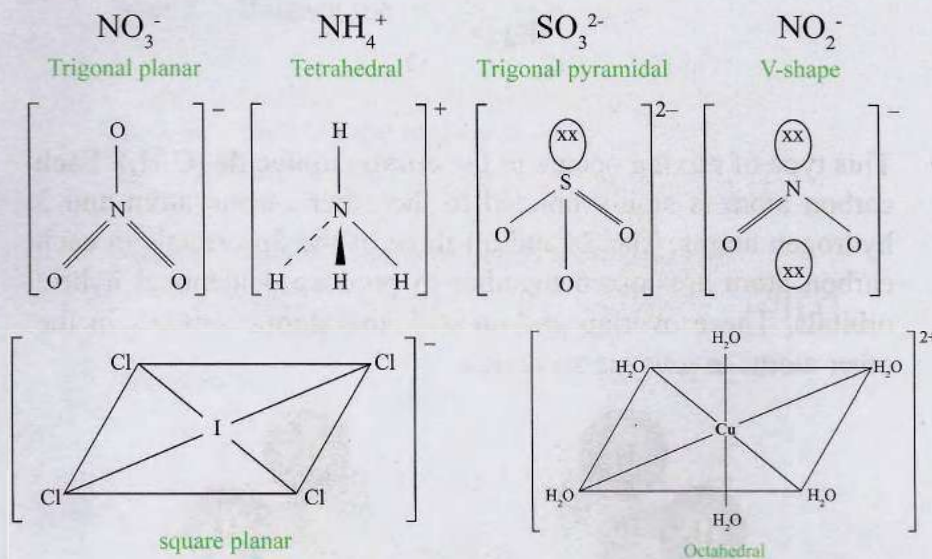


Fig. 2.27

Shapes of simple organic compounds

Carbon has the ability to mix and rearrange the four orbitals in the outer shell. This property is called **hybridization**. Carbon has the electronic configuration $1s^2 2s^2 2p^2$ and can promote an electron from the 2s orbital to the empty 2p orbital. Since both the 2s and the 2p subshells are half-filled, the excited state is relatively stable.

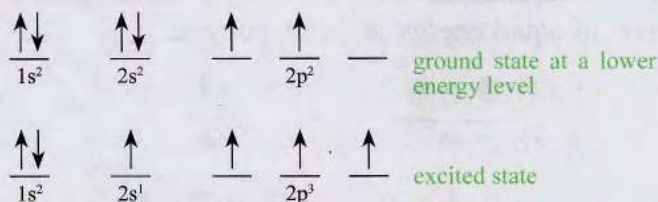
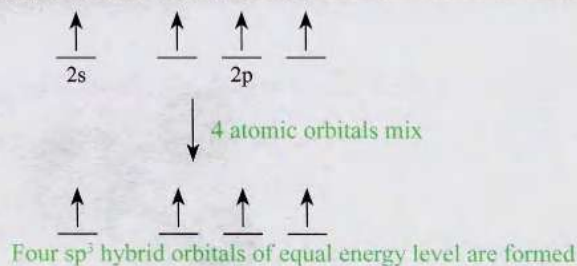


Fig. 2.28

Two or more atomic orbitals can mix to create new orbitals of equal energy called **hybrid orbitals**. If the s orbital and all three p orbitals mix, then four hybrid orbitals of equal energy level are formed. This type of mixing is called **sp^3 hybridization**.



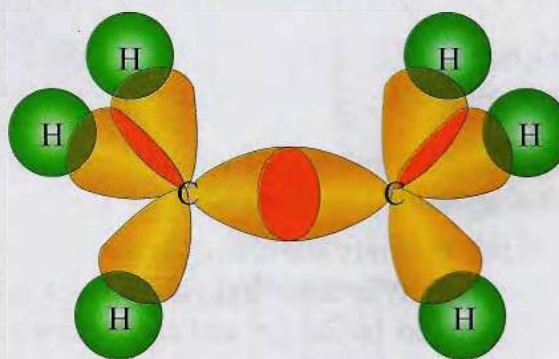
Fig. 2.29



four sp^3 hybrid orbitals of equal energy level on a carbon atom

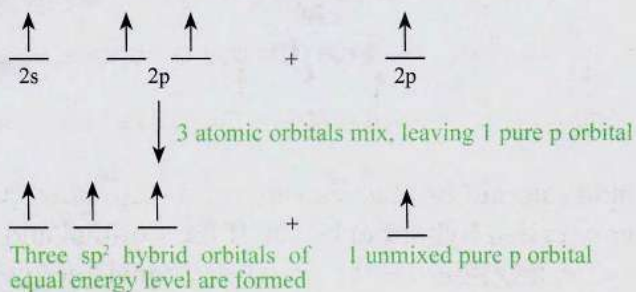
This type of mixing occurs in the **ethane molecule** (C_2H_6). Each carbon atom is singly bonded to the other carbon atom and 3 hydrogen atoms. The 2s and all three of the 2p orbitals in each carbon atom are mixed together to produce 4 identical hybrid orbitals. These overlap end-on with the atomic orbitals in the other atoms to give sigma bonds.

Fig. 2.30



atomic orbitals overlap to form sigma bonds

If the s orbital and two of the p orbitals mix, then, three **sp^2 hybrid orbitals** of equal energy level are formed.



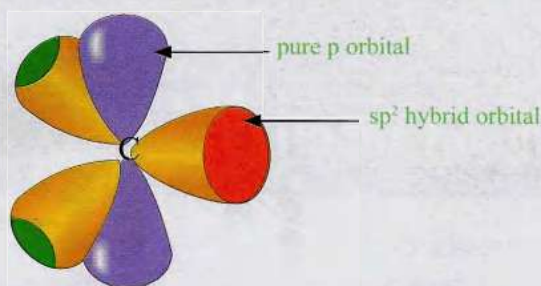


Fig. 2.31

This type of mixing occurs in the **ethene molecule** (C_2H_4). Each carbon is sigma bonded to the other carbon atom and 2 hydrogen atoms. The 2s and two of the 2p orbitals in each of the carbon atom are mixed together to give 3 identical hybrids. These overlap end-on to give three sigma bonds.

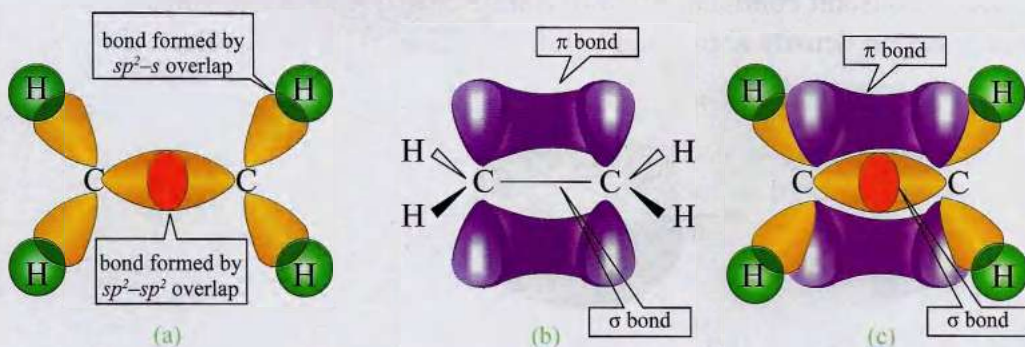


Fig. 2.32

The one electron remaining in each of the unmixed pure p orbital of the carbon atoms overlap sideways to form a pi bond above and below the plane of the sigma bonds.

Like ethene, the carbon atoms show sp^2 hybridization in **benzene** (C_6H_6). Each carbon atom forms three sp^2 hybrid orbitals and one unmixed pure p orbital. The hybrid orbitals overlap with the carbon and hydrogen atoms to form a planar hexagonal ring of sigma bonds.

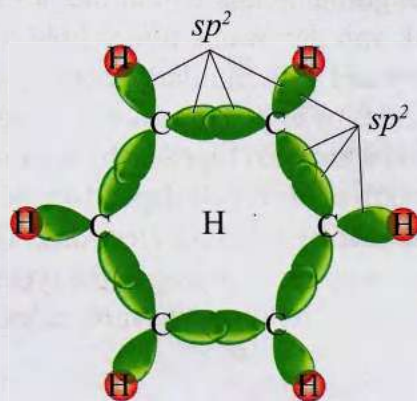


Fig. 2.33a

The remaining six unmixed p orbitals are all parallel to one another, each containing one electron. The p orbitals overlap



sideways at right angles to the planar hexagonal ring forming three pi bonds.

Benzene molecule

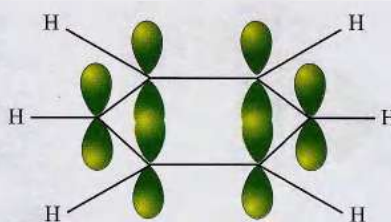


Fig. 2.33 b

Since there are two equivalent choices for the arrangements of the single and double bonds in the molecule, the structure is called a **resonance hybrid**. The three pi bonds are delocalized over the whole molecule i.e. the electrons are not in one particular place but are in constant continual motion. Hence they form circular rings of electron density above and below the plane of the molecule.

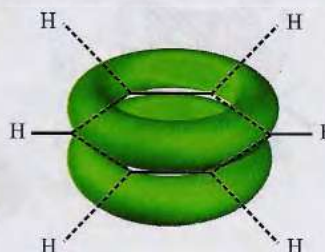


Fig. 2.33 c



CRYSTALLINE SOLIDS

A crystalline solid has a definite repeating arrangement of atoms, molecules or ions in a crystal. This arrangement is known as the crystal lattice. The hardness of a crystalline solid depends on the strength of the bonds that bind the atoms, molecules or ions in a crystal lattices. Diamond and silicon are hard and brittle because the bonds holding the lattices together are quite strong. In graphite, although the bonds within the hexagonal layers are strong, only weak van der Waals forces hold the layers. Hence graphite is slippery and soft. Similarly, only weak van der Waals forces hold molecules of iodine together causing it to sublime on heating. Metal atoms are held together by a cloud of delocalized electrons, the strength of the bonds depend on the size of the metal atoms and the number of bonding electrons. There are various types of solid structures each varying in the types of bonding and the forces of attraction holding the molecules together. These include:

- Simple molecular substances e.g. I_2
- Giant molecular substances e.g. SiO_2
- Ionic e.g. $NaCl$
- Metallic e.g. Cu

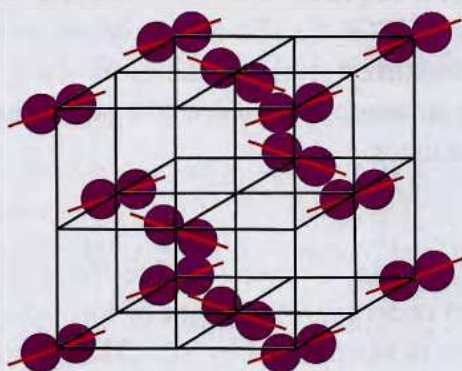


- Giant atomic e.g. diamond and graphite
- Hydrogen bonded e.g. ice

Simple molecular lattices

The atoms of a molecule are bonded covalently, however the separate molecules in the crystal lattice are held together by weak van der Waals forces of attraction. These weak intermolecular forces of attraction allow the molecules to separate from each other easily when heated. For example, if a small amount of energy is supplied to the solid iodine, the weak van der Waals forces of attraction are disrupted and the solid sublimates. The shiny black iodine crystals are converted into a purple vapour. The crystals are soft with low melting points and low boiling points. Simple molecular substances do not have any charged particles therefore they do not conduct electricity.

Fig. 2.34 below shows the arrangement of I_2 molecules in crystalline iodine. The molecules are arranged in a **face-centred** cubic crystal lattice. This means that there is a molecule at each corner of a cube and one at the centre of each face.



The face-centred cubic crystal lattice of I_2

Fig. 2.34

Giant molecular structures

Silicon dioxide (SiO_2) is an example of a giant molecular structure. Since silicon is a larger atom than carbon it can form only a single covalent bond with an oxygen atom. The p orbitals on the silicon and the oxygen are not close enough to allow sideways overlap to form a stable pi bond. Each silicon atom can therefore bond to four oxygen atoms. This gives rise to a giant covalent molecular structure in which each Si atom is bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms. The bonding between the atoms forms a three dimensional network in which the ratio between Si and O atoms is 1:2. Thus the formula of silicon dioxide, SiO_2 , is an empirical formula.



Iodine crystals

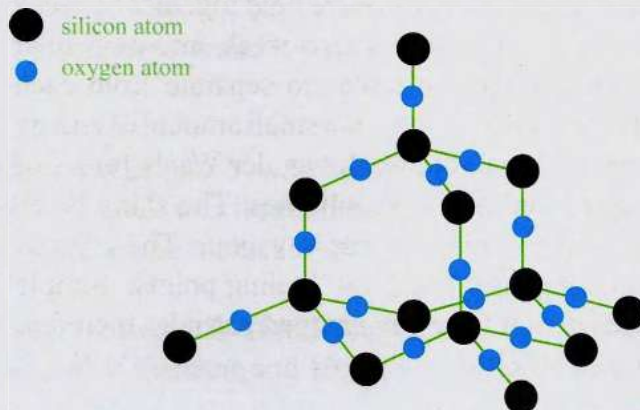




Quartz

Fig. 2.35
Silicon dioxide

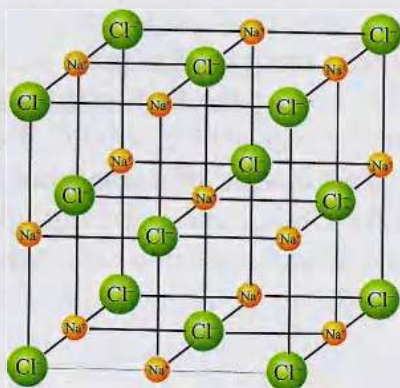
There are three crystalline forms of SiO_2 . These are quartz, tridymite and cristobalite. Of these, quartz has the simplest arrangement which is based on a diamond structure. Fig. 2.35 on the next page shows how each silicon atom is bonded to four oxygen atoms.



The covalent Si-O bond energy is 444 kJ mol^{-1} . The combined strength of all the covalent bonds in the macromolecular structure gives great strength and regularity to the structure. As such, a large amount of energy is required to break the structure apart. SiO_2 has a melting point of 1700°C . The macromolecular structure does not have any delocalized electrons therefore it is a non conductor of electricity. In automobiles fitted with spark plugs, SiO_2 is used as part of the insulator.

Ionic lattices

Sodium chloride forms a crystal lattice that has a giant ionic structure. It is an orderly arrangement of ions in a cubic pattern. Each sodium ion is surrounded by six chloride ions while each chloride ion is surrounded by six sodium ions. Thus sodium chloride is described as being 6:6 co-ordinated. The repulsion between ions of like charges is outweighed by the attraction between the oppositely charged ions resulting in strong electrostatic forces of attraction which holds the lattice together. Thus sodium chloride has a high melting and boiling point. It is also hard and brittle such that when a force is applied, the like charges repel each other resulting in the crystal being shattered.



(a) Sodium chloride crystal lattice

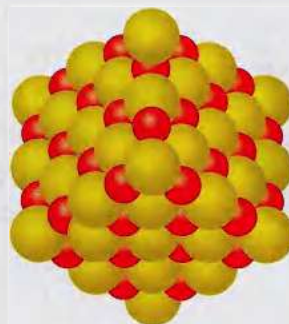


Fig. 2.36

(b) a space-filling model of the structure of sodium chloride

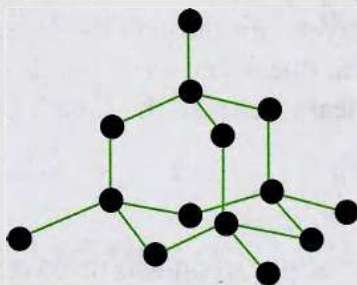
Sodium chloride is soluble in water. The sodium ions are attracted to the lone pairs on water molecules to form co-ordinate bonds while hydrogen bonds are formed with negative ions and water molecules. These attractions between the water molecules and the ions are large enough to overcome the attractions between the ions themselves so making sodium chloride soluble in water.

Sodium chloride does not conduct electricity in the solid state because there are no free electrons and the ions have restricted motion and are not free to move. However it conducts electricity when molten or dissolved in water. The ions become free to move therefore mobile charge carriers are present to conduct electricity.

Giant atomic structures

These consist of atoms arranged in a giant structure. Carbon can exist as diamond, graphite and more recently the Buckminsterfullerene structure. Although these structures consist of the same element they have unique and differing properties.

The structure of diamond



In diamond, each carbon atom is covalently bonded to four other C atoms in a tetrahedral arrangement. The bond length (C-C) is 0.154 nm and the bond energy is 350 kJ mol⁻¹. Diamond is a



Diamond

Fig. 2.37



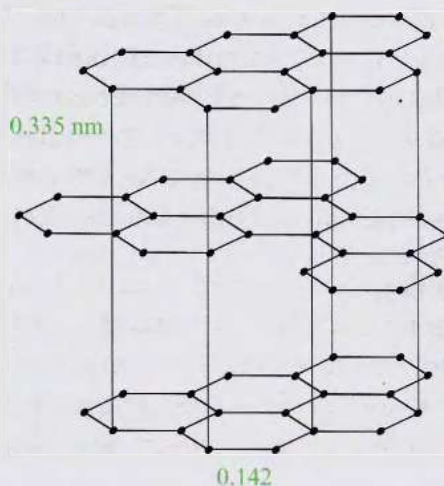


Graphite

Fig. 2.38

massive giant atomic structure consisting of only carbon atoms. This three dimensional network of C atoms confers great strength and rigidity to diamond, it being one of the hardest substance known to man. Its melting point is well above 3000°C . Being hard, diamond is used to make drill bits for oil exploration and diamond tipped tools are used for cutting and engraving glass. No free electrons are present and hence it is a non conductor of electricity.

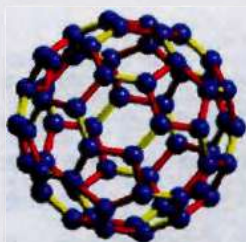
The structure of graphite



Graphite is also made up of pure carbon but each carbon atom is bonded covalently to three other carbon atoms. The carbon atoms are arranged in layers. The fourth electron of each carbon atom is in a p orbital which overlaps above and below the plane of the layer forming a delocalized electron cloud. This bond is so long (0.335nm) that the electrons in it are not bound and are free to move throughout the structure. Their movement is restricted to one plane, and so graphite conducts electricity but only in the plane between the layers not through the layers. Graphite is soft compared to diamond due to the weak bonds between the layers. It is used as a lubricant because the layers can slide over each other.

Buckminsterfullerene structure

In 1985 a new allotrope of carbon was discovered. It was a closed cage structure molecule containing 60 carbon atoms arranged like a soccer ball. This new molecule was named Buckminsterfullerene or 'bucky ball'. It got its name from a building in Montreal with a similar shape which was designed by Buckminster Fuller.



(a) Buckyball with red single and yellow double bonds



(b) C_{60} face-centered cubic crystal

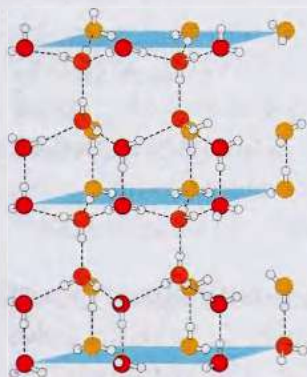
Fig. 2.39

Many similar molecules containing different numbers of carbon atoms have since been discovered. These substances are known as fullerenes.

Hydrogen bonded lattices

Ice has a well-defined tetrahedral structure in which each H_2O molecule is hydrogen bonded to four neighbouring H_2O molecules. Two of the H_2O molecules are hydrogen bonded to the oxygen atom on a central H_2O molecule while each of the hydrogen atoms on that central H_2O molecule is hydrogen bonded to neighbouring H_2O molecule.

This basic arrangement repeats itself in three dimensions to build the ice crystal. The hydrogen bonds are represented by the dashed lines in the structure of ice in fig. 2.40(a).



(a) open structure of ice



(b) hydrogen-bonded water molecules give ice its hexagonal symmetry as seen in snowflakes

Fig. 2.40

The arrangement of water molecules in ice creates an open structure which makes ice less dense than water. This is different from most compounds which are denser in the solid state than in the liquid state. Hydrogen bonding also gives rise to the high melting point of ice (0°C). This is much higher than a normal polar covalent molecule.



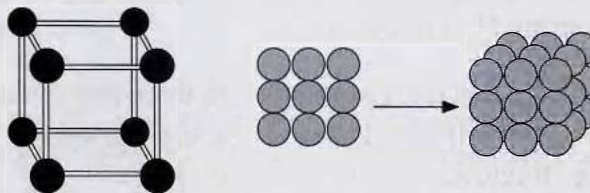
Metallic structure

Metals consist of layers of atoms packed as closely together as possible in a regular lattice. Each atom loses its outer electrons into a cloud of delocalized electrons which are free to move around the lattice. This gives rise to a strong structure with non-directional bonds. The layers allow slippage and the ions can easily re-bond in the cloud of electrons.

Metals atoms are thought of as identical spheres which adopt relatively simple structures. The most common crystal patterns associated with metals are simple cubic (s.c.), body-centered cubic (b.c.c.), cubic close-packed (c.c.p.) and hexagonal close-packed (h.c.p.).

In **simple cubic packing**, each atom is packed next to and directly on top of another sphere. Thus each atom touches four identical atoms in the same plane and one above and one below the plane. Hence it has a coordination number of 6.

Fig. 2.41



The simple cubic cell has an atom at each corner of a cube

A simple cubic structure is not an efficient way of using space. Only about half of the available space is actually occupied by the atoms, the rest is empty space. Polonium shows simple cubic packing.

In **body-centered cubic packing**, there are two different types of layers. The atoms in the second layer are packed above the holes in the first layer as shown in the figure Fig. 2.42. Atoms in the third layer are packed above the holes in the second layer and so on. The result is an ABABAB... pattern. An atom is arranged at each corner of a cube and one atom at the body center of the cube. The corner atoms do not touch one another but each touches the central atom along the diagonal of the cube. Each atom is surrounded by 8 other atoms hence the coordination number is 8.

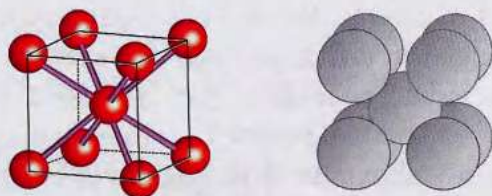


Fig. 2.42

The packing has about 68% efficiency in this lattice. The atoms occupy more space than in a simple cubic lattice. Example of metals with body-centered cubic packing are alkali metals and iron.

In the **cubic close-packed** structure, there are three different types of layers and the structure has an ABCABC... pattern. None of the atoms in each layer is directly above the other.

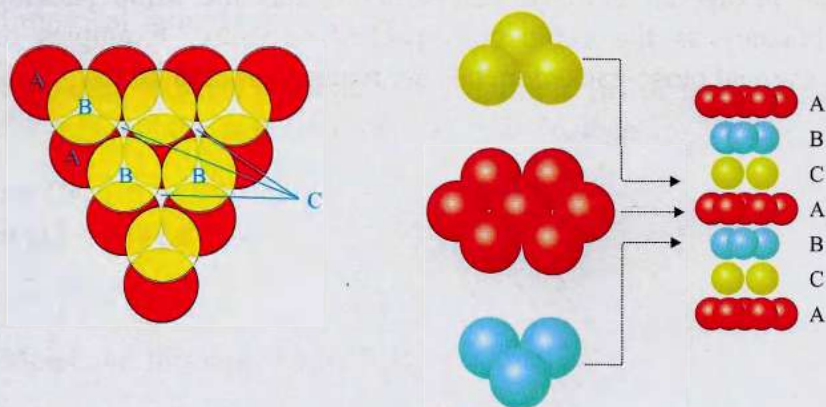
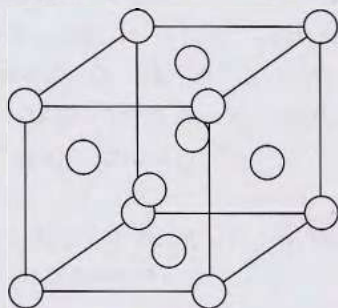


Fig. 2.43

An atom is arranged at each corner of a cube and one atom at the center of each of the faces of the cube. The cubic close-packed structure is also called a face-centered cubic (f.c.c.) structure. Each atom is surrounded by 12 other atoms hence the coordination number is 12. The atoms use about 74% of the available space for packing.



Face centred cubic structure

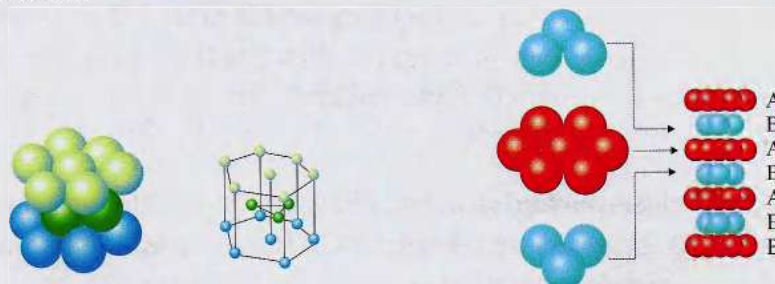
Metals with cubic close-packed structures tend to be malleable and ductile. Examples of cubic close-packed metals are gold, silver, copper and aluminium.

In the **hexagonal close-packed** structure, there are two different



types of layers of atoms. The top and bottom layers consist of six atoms arranged in a hexagon and one atom at the center of each of the hexagon. The middle layer consists of three atoms in between the top and bottom layers. The atoms in the third layer are positioned directly above the first. The result is an ABABAB... pattern.

Fig. 2.45



The hexagonal close-packed structure has the same packing efficiency as the cubic close-packed structure. Examples of hexagonal close-packed metals are magnesium and zinc.



Questions

1. Draw dot and cross diagrams to show the electronic structure of the following substances and predict the shapes of each molecule.
 - (a) AlF_3
 - (b) NH_3
 - (c) $\text{AlF}_3 \cdot \text{NH}_3$
2.
 - (a) Explain what is meant by the term ionic bonding.
 - (b) List three properties of ionic compounds
 - (c) Draw a dot and cross diagram to show the electronic structure of each atom in calcium fluoride.
3. Explain how metallic bonding accounts for the electrical conductivity of metals.
4. Describe the intermolecular forces of attraction in each of the following molecules.
 - (a) NH_3
 - (b) CO_2
 - (c) H_2O
 - (d) I_2
5. Account for the following observations as fully as you can:
 - (a) The boiling point of ammonia (-33°C) is higher than that of phosphine (-87°C).
 - (b) Nitrogen trichloride molecule is pyramidal in shape but aluminium chloride (AlCl_3) is trigonal planar in shape.
 - (c) Iodine is a solid crystal which sublimes.
 - (d) The boiling point of water is 100°C whereas that of argon is -186°C even though the relative molecular mass of each is 18.
 - (e) Carbon dioxide is a gas at room temperature whereas silicon dioxide is a high melting point solid even though both are covalent molecules.
 - (f) Sodium melts at 98°C whereas aluminium melts 660°C .
 - (g) The boiling point of water is 100°C whereas that of ammonia is -33°C .



6. The bond angles of methane, ammonia, and water are 109° , 107° and 105° respectively. Suggest an explanation for this variation in terms of repulsion between electron pairs.
7. Give an account of the bonding present in each of the following substances and show how their physical properties can be related to its bonding:
- iodine
 - silicon dioxide
 - sodium chloride
 - copper
 - diamond
 - graphite
8. Use the VSEPR theory to deduce the shapes and bond angles of the following molecules:
- PH_3
 - F_2O
 - SiH_4
 - H_2S
 - H_3O^+
 - NF_3
 - CF_4
 - SCl_2
9. Carbon has the ability to mix to create new hybrid orbitals. Describe the shapes of the following organic molecules in terms of their hybrid orbitals:
- ethane
 - ethene
 - benzene



The mole concept originated in the nineteenth century by an Italian chemist named Amadeo Avogadro. He stated that equal volumes of gases at the same temperature and pressure contain the same number of molecules. Although he had no idea what the number was, his hypothesis did eventually lead to the determination of the number 6.02×10^{23} as the number of particles in one mole of a substance which is called the Avogadro's number.

To simplify this concept, just as you would always assume that twelve of anything is called a dozen, twenty is called a score, one hundred is called a century, one hundred and forty four is called a gross, there will always be 6.02×10^{23} particles in 1 mole of any substance. Therefore *a mole is defined as the amount of substance that contains as many particles as there are carbon atoms in 12g of carbon-12 isotope.*



Amadeo Avogadro



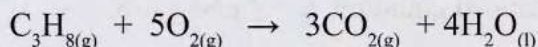
APPLICATION OF AVOGADRO'S LAW

Interpreting gaseous volumes directly from the balanced equation

The balanced equation indicates the number of molecules as well as the number of moles of reactants and products that are involved in the reaction. According to Avogadro's law, equal volumes of gases measured at the same temperature and pressure contain the same number of molecules. Therefore number of molecules can be replaced by volumes in the equation.

Example 1

What volume of carbon dioxide is produced when 100cm^3 of propane is completely burnt in oxygen? All volumes are measured at the same temperature and pressure.



From the equation,

1 molecule of propane produces 3 molecules of carbon dioxide

Using Avogadro's law,



One mole of carbon (12g)



1 volume of propane produces 3 volumes of carbon dioxide

Thus 100 cm³ of propane produces 300 cm³ of carbon dioxide at the same temperature and pressure.

Using gaseous volumes to determine an unknown formula and the equation for a reaction

By measuring the volume of reactants and products, the number of molecules taking part or produced in a reaction can be determined. This can be used to work out the formula of an unknown compound and the equation for the reaction.

Example 2

10 cm³ of an unknown hydrocarbon, C_xH_y, required 60 cm³ of oxygen for complete combustion. 40 cm³ of carbon dioxide was produced. Find the formula of the unknown hydrocarbon and write the equation for the reaction. All volumes were measured at the same temperature and pressure.

10 cm³ of C_xH_y requires 60 cm³ of oxygen to produce 40 cm³ of carbon dioxide

Using Avogadro's law

10 molecules of C_xH_y require 60 molecules of oxygen to produce 40 molecules of carbon dioxide

Therefore 1 molecule of C_xH_y requires 6 molecules of oxygen to produce 4 molecules of carbon dioxide



The number of hydrogen can be calculated indirectly from the number of oxygen. Since the number of oxygen on the left is 12, there must be a total of 12 on the right. 8 of those are in the 4CO₂, so there are 4 in the H₂O. Therefore there must be 4H₂O.



From the balanced equation, x = 4 and y = 8

The hydrocarbon is C₄H₈

The equation for the reaction is C₄H₈ + 6O₂ → 4CO₂ + 4H₂O



Determination of molar mass using molar volume

1 mole of any gas contains the same number of particles and occupies the same volume at the same temperature and pressure. This is referred to as the molar volume. The molar volume changes with temperature and pressure.

Molar volume of a gas at room temperature and pressure (rtp) is 24 dm^3 .

Molar volume of a gas at standard temperature and pressure (stp) is 22.4 dm^3 .

Thus it is possible to calculate the molar mass from a given volume of gas.

The molar mass is the mass of 1 mole of a substance expressed in grams. It is the mass of a substance containing 6.02×10^{23} particles of that substance.

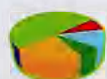
Example 3

0.367 g of a gas occupies 200 cm^3 at rtp, calculate the molar mass of the gas.

1 mole of gas occupies 24 dm^3 ($24\,000 \text{ cm}^3$).

200 cm^3 of gas weighs 0.367 g

$24\,000 \text{ cm}^3$ of gas will weigh $\frac{(0.367 \times 24\,000)}{200}$
 $= 44 \text{ g mol}^{-1}$



CHEMICAL EQUATIONS

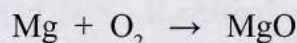
Writing equations

The chemical equation is a symbolic statement of what occurs in a chemical reaction. To write an equation you need to:

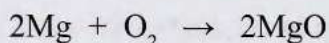
- Know the names of the reactants and products. For example

Magnesium + oxygen $\rightarrow$ magnesium oxide

- Know the formulae of the reactants and products.



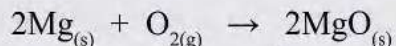
- Balance the equation by making the number of atoms of each element the same on both sides of the equation.



Remember never to alter any formula in balancing equations.

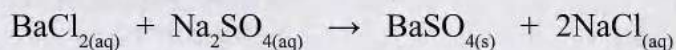


- Include state symbols

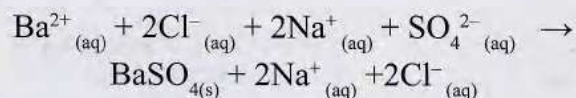


Ionic equations

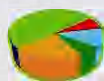
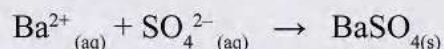
An ionic equation only shows the ions which take part in the reaction and ignore the ions which are unchanged in the reaction (spectator ions). The reaction between barium chloride and sodium sulphate can be written as



Barium chloride, sodium sulphate and sodium chloride exist as discrete ions in aqueous solution, thus the reaction can be represented as



$\text{Na}^{+}_{(aq)}$ and $\text{Cl}^{-}_{(aq)}$ ions appear unchanged on either side of the equation and take no part in the reaction. These are spectator ions and are cancelled out of the equation so that the ionic equation is written as



CALCULATIONS USING CHEMICAL EQUATIONS

A balanced equation can be used to give a quantitative relationship between reactants and products in terms of moles, mass, number of molecules or volumes.

Example 1

Potassium nitrate decomposes on heating according to the equation



When 5.05 g of potassium nitrate is heated, find

- the mass of potassium nitrite produced
- the volume of oxygen gas produced at rtp.
- the number of molecules of O_2 produced.

$$1 \text{ mole } \text{KNO}_3 = 101 \text{ g}$$

$$1 \text{ mole } \text{KNO}_2 = 85 \text{ g}$$

$$1 \text{ mole } \text{O}_2 \text{ occupies } 24 \text{ dm}^3 \text{ at rtp.}$$



From the equation,

(a) 2 moles KNO_3 produces 2 moles KNO_2

202 g KNO_3 produces 170 g KNO_2

$$\begin{aligned} 5.05 \text{ g } \text{KNO}_3 \text{ will produce } & \frac{(170 \times 5.05)}{202} \\ & = 4.25 \text{ g} \end{aligned}$$

(b) 2 moles KNO_3 produces 1 mole O_2

202 g KNO_3 produces 24 dm³ O_2 at rtp

$$\begin{aligned} 5.05 \text{ g } \text{KNO}_3 \text{ will produce } & \frac{(24 \times 5.05)}{202} \\ & = 0.6 \text{ dm}^3 \end{aligned}$$

(c) 101 g KNO_3 = 1 mole

$$\begin{aligned} 5.05 \text{ g } \text{KNO}_3 &= \frac{5.05}{101} \\ &= 0.05 \text{ mole} \end{aligned}$$

2 moles KNO_3 produces 1 mole O_2

0.05 mole KNO_3 will produce 0.025 mole O_2

$$\begin{aligned} 1 \text{ mole } \text{O}_2 &= 6.02 \times 10^{23} \text{ molecules} \\ 0.025 \text{ mole } \text{O}_2 &= 0.025 \times 6.02 \times 10^{23} \text{ molecules} \\ &= 1.505 \times 10^{22} \text{ molecules} \end{aligned}$$

Example 2

20 cm³ of 2 mol dm⁻³ H_2SO_4 reacts with excess Mg according to the equation



(a) Find the mass of magnesium sulphate produced in the reaction.

(b) Find the volume of H_2 gas produced at rtp.

The number of moles of H_2SO_4 used in the reaction

1000 cm³ contains 2 moles H_2SO_4

$$\begin{aligned} 20 \text{ cm}^3 \text{ will contain } & \frac{(2 \times 20)}{1000} \\ & = 0.04 \text{ mole} \end{aligned}$$



From the equation,

- (a) 1 mole H_2SO_4 produces 1 mole MgSO_4
0.04 mole H_2SO_4 will produce 0.04 MgSO_4

$$\begin{aligned}1 \text{ mole } \text{MgSO}_4 &= 120 \text{ g} \\0.04 \text{ mole } \text{MgSO}_4 &= 120 \times 0.04 \\&= 4.8 \text{ g}\end{aligned}$$

- (b) 1 mole H_2SO_4 produces 1 mole H_2 at rtp
0.04 mole H_2SO_4 will produce 0.04 mole H_2

$$\begin{aligned}1 \text{ mole } \text{H}_2 &= 24 \text{ dm}^3 \text{ at rtp} \\0.04 \text{ mole } \text{H}_2 &= 24 \times 0.04 \\&= 0.96 \text{ dm}^3\end{aligned}$$



EMPIRICAL AND MOLECULAR FORMULAE

The *empirical formula* is the simplest whole number atomic ratio of the elements present in a compound.

The *molecular formula* is a simple multiple of the empirical formula. It shows the actual number of atoms of the different elements in 1 molecule of the compound.

Example 1

What is the empirical formula of compound which contains 43.4 % Na, 11.3 % C and 45.3 % O by mass?

Element	Na	C	O
Percentage	43.4 %	11.3 %	45.3 %
Combining masses in 100 g	43.4	11.3	45.3
Number of moles	$\frac{43.4}{23}$	$\frac{11.3}{12}$	$\frac{45.3}{16}$
	= 1.89	= 0.94	= 2.83
Ratio of moles	2	1	3

Empirical formula is Na_2CO_3

Example 2

A hydrocarbon X has a relative molecular mass of 56. Complete combustion of 0.1 g of X give 0.316 g of CO_2 and 0.128 g of H_2O . Find the empirical and molecular formulae of X.

Mass of C and H in 0.1 g of X



44 g CO₂ contains 12 g C

0.316 g CO₂ contains $\frac{(12 \times 0.316)}{44} = 0.086$ g C

18 g H₂O contains 2 g H

0.128 g H₂O contains $\frac{(2 \times 0.128)}{18} = 0.014$ g H

Element	C	H
Mass ratio	0.086	0.014
Number of moles	$\frac{0.086}{12}$	$\frac{0.014}{1}$
	= 0.0072	= 0.014
Mole ratio	1	2

Empirical formula of X is CH₂

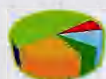
Since the molecular formula is a multiple (n) of the empirical formula and the molecular mass of X is 56, then

$$n(\text{CH}_2) = 56$$

$$n(12 + 2) = 56$$

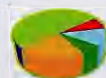
$$n = \frac{56}{14} = 4$$

Molecular formula of X is C₄H₈.



TITRATION

This involves measuring the volume of a solution of known concentration (the **standard solution** or **titrant**) which is required to react quantitatively with another solution of unknown concentration (**analyte**). Generally, the titrant is added from a burette to a known volume of the analyte until the reaction is complete. An indicator is usually used to signal the end of the reaction. The concentration of the unknown solution can then be determined from the stoichiometry of the reaction and the volume of standard solution used in the reaction. Substances of known purity are used to prepare standard solutions. These substances are called **primary standards**.



PRIMARY STANDARDS

A primary standard is a substance of high purity that is used to prepare the concentration of the standard solution in the volumetric analysis. It provides a reference to determine unknown concentrations.



Primary standards should have the following properties:

- **High purity** – it should have a purity of at least 99.98%.
- **Stable towards air** – the composition should not be altered on exposure to air. This means it should not be oxidized by air, react with carbon dioxide or absorb moisture from air.
- **Absence of water of crystallization** – it should be stable to drying. The composition should not change when heated.
- **Relatively large formula weight** – this minimizes the relative errors associated with weighing.
- **It should be soluble in titration medium.**

Examples of primary standards are NaHCO_3 , Na_2CO_3 , KIO_3 and $(\text{COOH})_2$.

Secondary standards are usually solutions of unknown concentrations that are standardized in the laboratory against primary standards.



ACID-BASE TITRATION

Acid-base titrations are used in volumetric analyses to find the concentration of an acid or base. An indicator is usually added which changes colour at the end of the reaction. The colour change on completion of the reaction is called the **end-point** of the reaction (see pages 163 - 165).

Example 1

25 cm³ of 0.1 mol dm⁻³ NaOH solution required 20 cm³ of dilute sulphuric acid for neutralization. Calculate the molar and mass concentration of the sulphuric acid.

1000 cm³ contains 0.1 mole of NaOH

$$\begin{aligned} 25 \text{ cm}^3 \text{ contains } & \frac{(0.1 \times 25)}{1000} \\ & = 0.0025 \text{ mole NaOH} \end{aligned}$$

Equation for the reaction



2 moles NaOH reacts with 1 mole H_2SO_4

$\therefore$ 0.0025 mole NaOH reacts with 0.00125 mole H_2SO_4



20 cm³ contains 0.00125 mole H₂SO₄

$$\begin{aligned} 1000 \text{ cm}^3 \text{ contains } & \frac{(0.00125 \times 1000)}{20} \\ & = 0.0625 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 \end{aligned}$$

$$1 \text{ mole H}_2\text{SO}_4 = 98 \text{ g}$$

$$\begin{aligned} 0.0625 \text{ mole H}_2\text{SO}_4 & = 0.0625 \times 98 \\ & = 6.125 \text{ g dm}^{-3} \end{aligned}$$

REDOX TITRATION

Redox titrations are based on the redox reaction between the titrant and analyte. The titrant oxidizes or reduces the analyte in the titration. Since electron transfer occurs from one atom to another, a redox indicator or a potentiometer can be used to signal the end-point of the reaction.

A redox indicator undergoes a definite colour change at a specific electrode potential e.g. phenanthroline and methylene blue. Titrations with transition metal compounds do not require an external indicator as they are self-indicating since varying oxidation numbers of transition metals show colour changes in their compounds, e.g. KMnO₄ and K₂Cr₂O₇.

Example 2

25 cm³ of 0.04 mol dm⁻³ sodium sulphite solution required 20 cm³ of 0.02 mol dm⁻³ KMnO₄ for complete oxidation. Calculate the number of moles of sodium sulphite which react completely with 1 mole of KMnO₄.

1000 cm³ solution contains 0.04 moles Na₂SO₃

$$\begin{aligned} 25 \text{ cm}^3 \text{ solution contains } & \frac{(0.04 \times 25)}{1000} \\ & = 0.001 \text{ mole Na}_2\text{SO}_3 \end{aligned}$$

1000 cm³ solution contains 0.02 mole KMnO₄

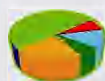
$$\begin{aligned} 20 \text{ cm}^3 \text{ solution contains } & \frac{(0.02 \times 20)}{1000} \\ & = 0.0004 \text{ mole KMnO}_4 \end{aligned}$$

0.0004 mole KMnO₄ reacts with 0.001 mole Na₂SO₃

$$1 \text{ mole KMnO}_4 \text{ reacts with } \frac{0.001}{0.0004} = 2.5 \text{ moles Na}_2\text{SO}_3$$



Hence the balance equation for the reaction is



BACK TITRATION

A back titration is an indirect titration method where the concentration of an analyte is found by reacting it with an excess known amount of reagent and then titrating the unreacted reagent with a standard solution. The titration results with the standard solution can be used to calculate the amount of unreacted reagent which can then be used to find the concentration of the analyte.

Back titrations are useful in reactions where

- the analyte is insoluble in water
- the analyte is volatile
- the end-point is not sharp
- the reaction is slow

Example 3

In an experiment to determine the amount of calcium carbonate in a typical antacid tablet, 25 cm³ of 1 mol dm⁻³ HCl was added to a conical flask with one antacid tablet in it. The solution was warmed gently until all the effervescence has ceased. After cooling for a few minutes, the solution was titrated with 0.5 mol dm⁻³ NaOH solution using phenolphthalein indicator. It was found that 30 cm³ of the NaOH was required to neutralize the unreacted HCl.

- Calculate the number of moles of HCl in the 25 cm³ of acid used.
- Find the number of moles of NaOH used in the titration.
- How many moles of HCl reacted with the NaOH in the titration?
- How many moles of HCl reacted with the CaCO₃ in the antacid?
- Find the number of moles of CaCO₃ in the antacid.
- Determine the mass of CaCO₃ present in the antacid tablet.



Calcium carbonate is a sparingly soluble salt therefore the antacid tablet is dissolved in excess acid and is back titrated with sodium hydroxide to determine the amount of calcium carbonate present.

(i) The number of moles of HCl in the 25 cm³ of acid

$$\begin{aligned} 1000 \text{ cm}^3 &\text{ contained 1 mole of HCl} \\ 25 \text{ cm}^3 &\text{ contained } (1 \times 25) \\ &\quad 1000 \\ &= 0.025 \text{ mole HCl} \end{aligned}$$

(ii) The number of moles of NaOH used in the titration

$$\begin{aligned} 1000 \text{ cm}^3 &\text{ contained 0.5 mole of NaOH} \\ 30 \text{ cm}^3 &\text{ contained } (0.5 \times 30) \\ &\quad 1000 \\ &= 0.015 \text{ mole NaOH} \end{aligned}$$

(iii) The number of moles of HCl reacted with the NaOH in the titration

Equation for reaction



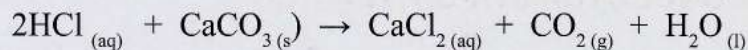
1 mole NaOH reacted with 1 mole HCl
 $\therefore$ 0.015 mole NaOH reacted with 0.015 mole HCl

(iv) The number of moles of HCl reacted with the CaCO₃ in the antacid

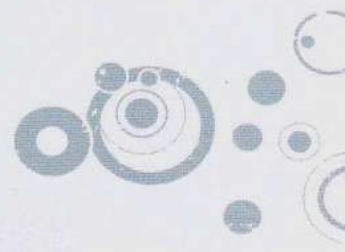
$$0.025 - 0.015 = 0.01 \text{ mole HCl}$$

(v) The number of moles of CaCO₃ in the antacid

Reaction of the CaCO₃ with HCl



2 moles HCl reacted with 1 mole CaCO₃
 $\therefore$ 0.01 mole HCl reacted with 0.005 mole CaCO₃



(vi) The mass of CaCO_3 present in the antacid tablet.

$$\begin{aligned} 1 \text{ mole } \text{CaCO}_3 &= 100 \text{ g} \\ 0.005 \text{ mole } \text{CaCO}_3 &= 100 \times 0.005 \\ &= 0.5 \text{ g } \text{CaCO}_3 \end{aligned}$$



THERMOMETRIC TITRATION

Another method that can be used to determine the neutralization point is the temperature change of the reactants. This is known as thermometric titration. Since neutralization is an exothermic reaction, the maximum temperature reached marks the end point of the reaction. A plot of the graph of temperature versus the total volume of the acid added can be used to find the neutralization point. Straight lines with best fit are drawn and extended until they intersect. The point at which the two lines meet corresponds to the volume of acid needed for the neutralization and the maximum temperature (see Fig. 3.1). Because enthalpy change is a universal characteristic of chemical reactions, thermometric endpoint can be used for a wide range of titration types such as acid/base, redox, complexometric (EDTA) and precipitation.

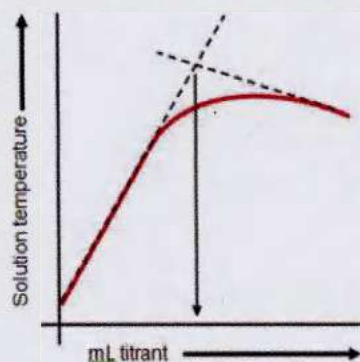


Fig. 3.1



POTENTIOMETRIC TITRATION

Potentiometric titration monitors the change in concentration of a solution by measuring the potential of a solution. A pH meter can be used for this titration. A pH meter consists of a voltmeter which is connected to two electrodes, one is a reference electrode and the other is an indicator electrode. When the electrodes are placed in the solution, they create a potential difference which can be detected by the voltmeter. In an acid/base titration, the more $[\text{H}^+]$ gives a higher voltage and a lower pH. The potential can be measured in voltage or pH. The graph which is obtained by plotting the pH against the volume of the titrant is a titration curve (see page 164).



CONDUCTOMETRIC TITRATION

Conductometric titration uses a conductivity sensor to measure the change in conductivity of the solution as the titration proceeds. Conductivity can increase or decrease during a titration and this is associated with the change in concentration of ions in solution mainly H^+ and OH^- ions for acid/base reactions. This method can be used for coloured solutions which cannot use normal indicators.



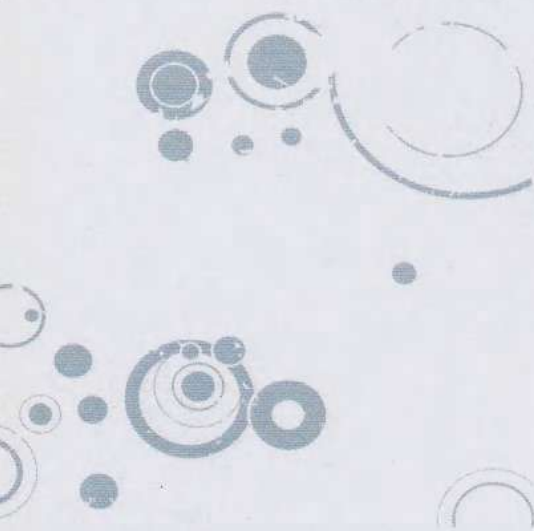


Questions

1. Define the following terms:
 - (a) mole
 - (b) empirical formula
 - (c) molecular formula
 - (d) Avogadro's law
2. A compound Z contains carbon, hydrogen and oxygen, and has a relative molecular mass of 46. Complete combustion of 1.0 g of Z give 1.91 g of CO_2 and 1.17 g of H_2O . Find the empirical formula and molecular formula of Z.
3. In a titration involving potassium manganate (VII) and Fe^{2+} ions, 25 cm^3 of an aqueous solution containing Fe^{2+} ions required 22.40 cm^3 of 0.02 mol dm^{-3} potassium manganate (VII) for complete reaction. The equation for the reaction is
$$5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$$
 - (a) Find the number of moles of MnO_4^- ions used in the reaction.
 - (b) Calculate the number of moles of Fe^{2+} ions in 25 cm^3 of solution
 - (c) Calculate the concentration of Fe^{2+} in mol dm^{-3} .
4. 40 cm^3 of a solution of phosphoric acid containing 0.98 g dm^{-3} reacted with 50 cm^3 of a solution containing 0.64 g dm^{-3} sodium hydroxide.
 - (a) Calculate the number of moles of phosphoric acid used in the reaction.
 - (b) Calculate the number of moles of sodium hydroxide used in the reaction.
 - (c) Determine the number of moles of sodium hydroxide that will react with 1 mole of phosphoric acid.
 - (d) Using the answer to (c) above, derive an equation for the reaction between sodium hydroxide and phosphoric acid.



5. Potassium chlorate (V), KClO_3 , decomposes on heating to potassium chlorate (VII), KClO_4 , and potassium chloride. Calculate the maximum number of moles of potassium chlorate (VII) which could be produced from 0.1 mole of potassium chlorate (V).
6. When 0.112 dm^3 of an organic compound Y was burnt in excess oxygen, 0.88 g of carbon dioxide was formed at s.t.p. How many carbon atoms are there in one molecule of Y?
7. Calculate the volume of oxygen required for the complete combustion of a mixture of 10 cm^3 of methane and 10 cm^3 of ethane at r.t.p.
8. Find the volume of 0.1 mol dm^{-3} aqueous silver nitrate required to react completely with 20 cm^3 of 0.2 mol dm^{-3} solution of calcium chloride.



Redox Reactions



Rusting iron

In earlier times chemists used the term oxidation to mean the addition of oxygen to a substance or the removal of hydrogen from a substance. The term reduction meant the addition of hydrogen to a substance or the removal of oxygen from a substance. Nowadays oxidation and reduction reactions or *redox* reactions are recognized in terms of electron transfer. Many chemical reactions such as the rusting of iron, the burning of fuels, respiration and photosynthesis involve redox reactions.



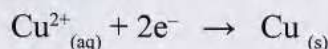
OXIDATION AND REDUCTION

Oxidation is commonly defined as the loss of electrons or an increase in oxidation state. Take for example, the chemical reaction



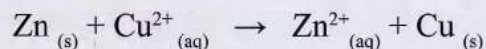
Here solid zinc has lost two electrons to form the Zn^{2+} cation. There is a change in oxidation state from zero to +2, therefore an increase in oxidation state. The zinc atom is oxidized to zinc ion.

Reduction is commonly defined as the gain of electrons or a decrease in oxidation number. Consider the example



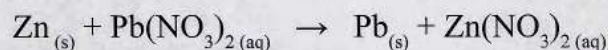
The Cu^{2+} cation has gained two electrons to form the Cu atom. The oxidation state has changed from +2 to 0, showing a decrease in oxidation state. The Cu^{2+} cation is reduced to Cu atom.

Oxidation and reduction does not occur independently, they always occur together. Oxidation and reduction reactions are usually written as balanced ionic half equations. The two ionic half equations are then merged together to generate a full equation. The two equations above can be written as the full equation below.

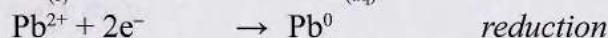
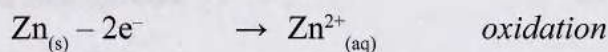


Similarly, the following redox reactions show the oxidation and reduction half equations.

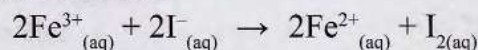




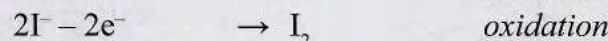
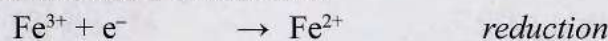
In this reaction the oxidation number of zinc changes from 0 to +2 and that of lead changes from +2 to 0.



In the redox reaction



Fe^{3+} is reduced and I^{-} is oxidized

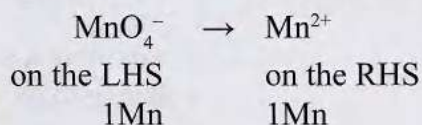


REDOX EQUATIONS

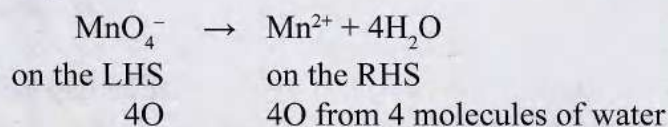
Writing a balanced half equation

The following rules must be applied when balancing half equations:

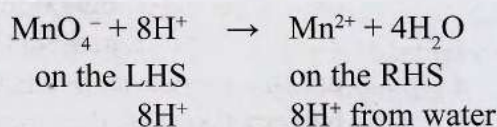
- (1) Balance the element that is being oxidized or reduced first.



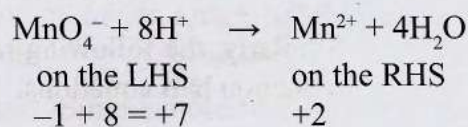
- (2) Add the correct number of moles of water to balance the oxygen ignoring the amount of H^+ contained in the water temporarily.



- (3) Add H^+ to balance the hydrogen as a result of the hydrogen added from water.

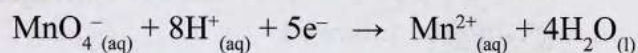


- (4) Finally, balance the charges by adding electrons to either side of the equation:



We therefore add five electrons on the left hand side to produce a +2 charge.

The equation is therefore:



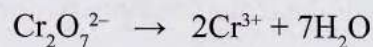
Example 2



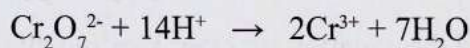
Step 1: Balance the Cr



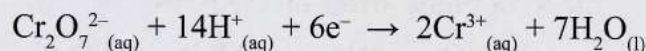
Step 2: Balance the oxygen with water



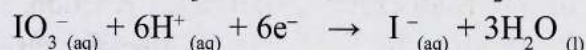
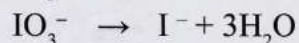
Step 3: Balance the hydrogen



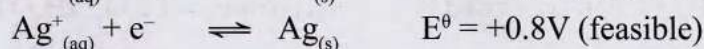
Step 4: Add electrons to balance the charges:



Example 3



Half equations are written as electrode reactions and usually as reduction reactions. There is an electrode potential value (E^0) given in volts associated with each equation. If the value given is positive then the reduction reaction is an energetically feasible reaction whereas a negative value is considered to be an energetically non-feasible reaction. For example



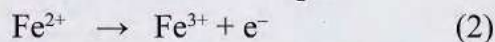
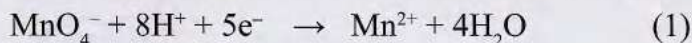
In these examples, reaction 1, and 3 are feasible. Reaction 3 is more feasible than reaction 1 while the negative value for reaction 2 indicates that it is not energetically feasible and will not take place under normal conditions.



Combining two half equations to give balanced equations

In order to write a balanced equation from half equations, the following rules must be followed:

- Write both equations to be combined in different lines.



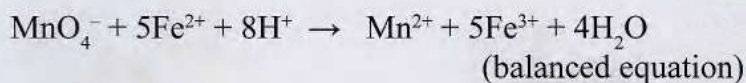
- Balance the electrons in each equation. In equation 2, multiply by 5.



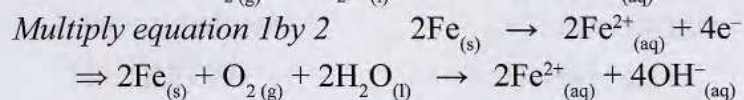
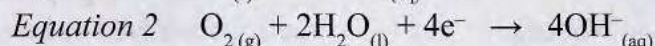
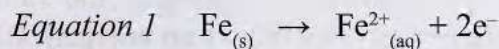
- Strike out the electrons from both equations.



- Add the equation together keeping all the species on the LHS of the arrow on the LHS and add all the species on the RHS of the arrow on the RHS.

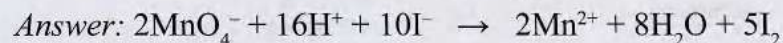
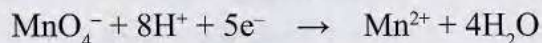


The rusting of iron is an example of a redox reaction. Solid iron loses electrons to form the Fe^{2+} cation while oxygen combines with water where it gains four electrons to form the hydroxide anion. The overall process can be summarized as shown below.



$\text{Fe}(\text{OH})_2$ is then converted to iron (III) oxide $\Rightarrow \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (rust).

Write a balanced equation for the following half equations:



Write half equations for the reaction between

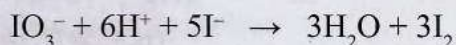
(i) I_2 and $\text{S}_2\text{O}_3^{2-}$ ($\text{S}_2\text{O}_3^{2-}$ is oxidized to $\text{S}_4\text{O}_6^{2-}$)

(ii) H_2O_2 and I^- in acid solution

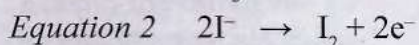
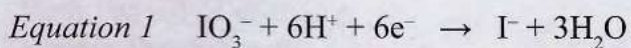
Note that all species on the LHS are converted to new species on the RHS. If a species is not converted to anything new (spectator ions), then it is removed from the equation. For example



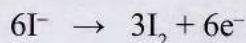
The I^- on the RHS is removed and one of the I^- on the LHS is removed giving



Consider this example



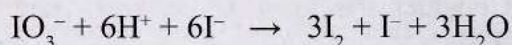
- First balance the electrons in equation 2 by multiplying by 3:



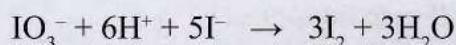
- Remove the electrons from both equations giving:



- Merge RHS of both equations and LHS of both equations:



- Finally remove one iodide ion from each side of the equation:

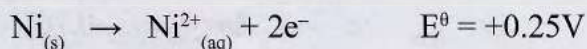


Using E^θ values to write chemical equations

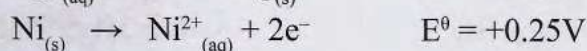
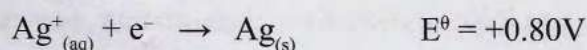
Electrode potential (E^θ) values are a great help in writing balanced equations for redox reactions. The E^θ values tell us the direction in which the half-equation proceeds. The more positive the E^θ value, the stronger is the ability of the substance to act as an oxidizing agent. For example,



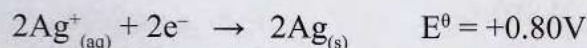
Equation 2 is not energetically feasible since the E^θ is negative. If the equation is reversed, the E^θ becomes positive and the reaction is then feasible.



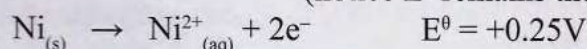
We can now merge the following two half equations to produce the full equation.



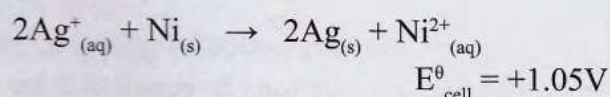
Balance the electrons



(notice E^θ remains the same)



Merge both half equations



An overall positive E^θ_{cell} tells us that the overall reaction is feasible.

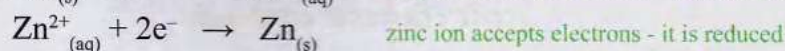
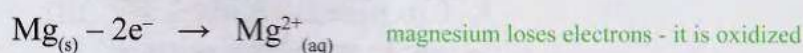


OXIDIZING AGENTS

An oxidizing agent is a substance which accepts electrons. As it accepts electrons, its oxidation state decreases and it becomes reduced. Consider the reaction between magnesium and zinc chloride below.

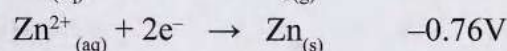
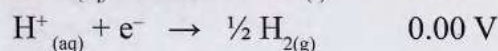
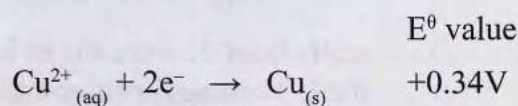


The ionic half equations are:



Therefore $\text{Zn}^{2+}_{(\text{aq})}$ is the oxidizing agent, it oxidizes Mg to $\text{Mg}^{2+}_{(\text{aq})}$ while itself was reduced to $\text{Zn}_{(\text{s})}$.

The strength of an oxidizing agent is measured by its ability to accept electrons. Standard electrode potential values are a direct measure of the oxidizing ability of substances. Consider the following electrode potentials:



The more positive the E^θ value, the stronger is the ability of the substance to act as an oxidizing agent. Therefore in the prior list, Cu^{2+} is the most powerful oxidizing agent followed by H^+ and then Zn^{2+} as is reflected by their E^θ values.

The standard electrode potentials for some half equations are given below. The stronger oxidizing agents have the more positive E^θ values.

Table 4.1

Some common oxidizing agents and their corresponding E^θ values

Equation	E^θ/V
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+ 2.87
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+ 1.51
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+ 1.36
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+ 1.33
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+ 1.09
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+ 0.77
$2\text{H}^+ + \text{O}_2 + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	+ 0.68
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+ 0.54
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+ 0.34



REDUCING AGENTS

A reducing agent is a substance which has the ability to donate electrons. On giving up electrons, its oxidation state increases and it is oxidized. Reducing agents also range in their ability to donate electrons. For example, metals tend to give up electrons and this in turn is determined by their ionization energy values. Electrode potential values are also good indicators of the reducing ability of a substance.

Table 4.2

Some common reducing agents and their corresponding E^θ values

Equation	E^θ/V
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}_{(s)}$	- 0.13
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}_{(s)}$	- 1.66
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}_{(s)}$	- 0.44
$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}_{(s)}$	- 2.37
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}_{(s)}$	- 2.71
$\text{K}^+ + \text{e}^- \rightarrow \text{K}_{(s)}$	- 2.92

From table 4.2 above, the more negative the E^θ value, the stronger is the ability of the substance to act as a reducing agent. Therefore stronger reducing agents have more negative E^θ values.





TEST FOR OXIDIZING AND REDUCING AGENTS

In redox reaction, the electrons lost from the reducing agent are accepted by the oxidizing agent. Therefore an oxidizing agent which gives a vivid colour change when reduced can be used to test for a reducing agent and vice versa.

Tests for oxidizing agents

- An oxidizing agent liberates I_2 from KI.



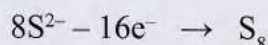
Solution changes from colourless to brown.

- An oxidizing agent oxidizes $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$



Solution changes from pale green to yellow-brown.

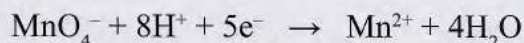
- An oxidizing agent precipitates sulphur from H_2S .



Solution forms a yellow suspension of sulphur.

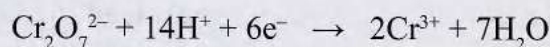
Tests for reducing agents

- A reducing agent decolourizes acidified potassium manganate (VII).



Colour changes from purple to colourless.

- A reducing agent reduces acidified dichromate (VI) ions to chromium (III) ions.



Colour changes from orange to green.



SIMPLE DISPLACEMENT REACTION

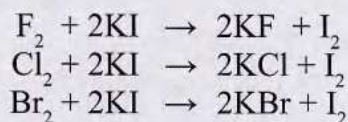
Displacement reactions involve one element or group in a compound being replaced by another element or group. Displacement reactions depend on the oxidizing and reducing abilities of substances and whether the substances are metals or non-metals.

Elements are arranged in terms of oxidizing and reducing abilities in the electrochemical series. Elements higher in the series are stronger reducing agents while those lower in the series are stronger oxidizing agents. Two types of displacement reactions are considered next.

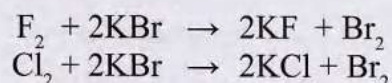


Non-metals

The more reactive non-metals are lower in the series and can displace or oxidize the less reactive non-metal ion. The equations below show how iodide ions can be displaced or oxidized by fluorine, chlorine and bromine.



Bromide ions can be displaced or oxidized by fluorine and chlorine but not by iodine.



Chloride ions can be oxidized by fluorine but not bromine or iodine.



Fluorine is not oxidized by any of the halide ions.

The above reactions show that the order of oxidizing ability is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

Metals

The more reactive metals are higher in the series and can displace or reduce the ion of a metal lower in the series. Thus magnesium metal will displace or reduce zinc ions from a solution of its salt since magnesium is higher than zinc in the series.



Exercise

Use the table below to determine the order of reactivity of X, Y, Z and α .

Metals	Solution of nitrates	Observation
X	Nitrate of Y	Brown ppt formed from green solution
X	Nitrate of Z	No reaction
X	Nitrate of α	Gold precipitate formed
Y	Nitrate of X	No reaction
Y	Nitrate of Z	No reaction
Y	Nitrate of α	Gold precipitate formed

Solution

When X reacts with the cation of Y a displacement reaction occurs. Therefore X is a more powerful reducing agent than Y. X is higher than Y in the electrochemical series.



The metal iron nail displaces the blue Cu^{2+} ions from the CuSO_4 solution to form the brown metallic Cu.



When X reacts with the cation of α , it displaces the ions of α from solution. Therefore X is a more powerful reducing agent than α . X is higher than α in the electrochemical series.

When Y reacts with the cation of α , it displaces it from solution. Therefore Y is a more powerful reducing agent than α . Y is higher than α in the electrochemical series.

The cation of Z is not displaced by metal X or Y therefore it is the most powerful reducing agent.

Thus the order of increasing reactivity of the metals is α , Y, X and Z.

Reducing ability: $Z > X > Y > \alpha$

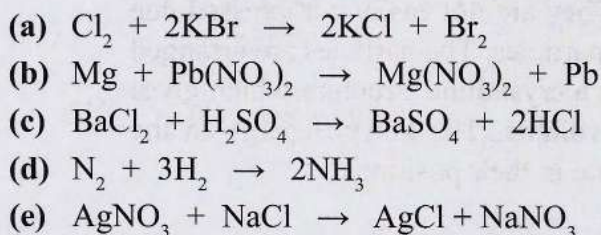
Oxidizing ability: $\alpha > Y > X > Z$





Questions

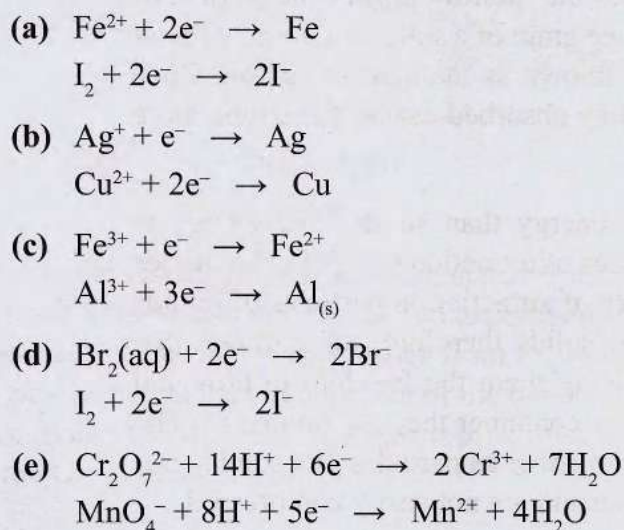
1. In the equations below, identify the redox reactions stating which species are oxidized and which are reduced.



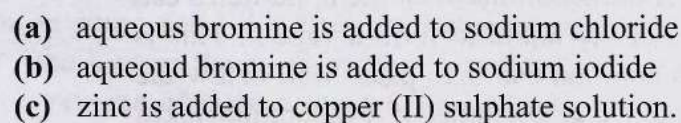
2. In the redox reactions identified in question (1) above, name the oxidizing and reducing agents.

3. Write two half-equations for the redox reactions named in question (1) above.

4. Write balanced equations for the following redox reactions by combining the half equations:



5. Describe the observations expected in the following reactions:



The kinetic theory of matter explains the extent to which particles move in solids, liquids and gases. In solids, the intermolecular forces of attraction are strong enough to keep particles close together and held in fixed positions. They are not easily compressed due to lack of space between the particles. The particles are arranged in an orderly fashion to form a crystalline structure which gives it definite shape as well as volume. The kinetic energy in the particles causes them to vibrate in their positions.



CHANGE OF STATE

The kinetic energy of particles in a solid increases as its temperature gradually increases. **Melting** starts when the energy the solid takes in is used to overcome the forces holding the particles together. The structure of the solid breaks down to form a liquid and the particles become free to move relative to each other. The temperature remains constant during melting and this constant temperature is called the **melting point**. The amount of energy required to convert one gram of a solid to a liquid without changing its temperature is known as the **heat of fusion**. Once melting is complete the energy absorbed causes the temperature to rise again.



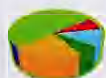
Candle wax melting

Liquids have more kinetic energy than solids. The energy is enough to overcome the forces of attraction which held particles in fixed positions. The forces of attraction in particles of liquids are not as strong as that of solids therefore, the particles can vibrate as well as rotate, giving them the freedom to flow and assume the shape of whatever container they are poured in. The particles are almost as close together as particles in a solid hence liquids have a definite volume and are not easily compressed.

When the kinetic energy of the particles in a liquid becomes greater than the forces of attraction between them, particles can escape from the surface of the liquid to form a vapour. This is called **evaporation**. Evaporation can take place well below the boiling point of the liquid e.g. perfume. If evaporation takes place in a close container, the molecules of the vapour exert a vapour pressure. As the vapour is confined over the surface of



the liquid, some will condense and re-enter the liquid. When the molecules reach a state of dynamic equilibrium, that is when the rate of evaporation is equal to the rate of condensation, the vapour pressure is known as the **saturated vapour pressure**. When the saturated vapour pressure becomes equal to the external pressure the liquid boils. This is called **vaporization**. The temperature at which the liquid boils is called the **boiling point** at that pressure. When boiling occurs the temperature remains constant as the energy is used to overcome the forces of attraction between the molecules.

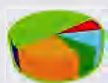


ASSUMPTIONS OF THE KINETIC THEORY

The kinetic theory of gases explains the extent to which particles move in a gas. It allows us to account for the behaviour of gases by making 5 basic assumptions. These are:

- 1. **The gas molecules are in a constant state of random motion.** The molecules move in a straight line until they collide with other molecules or the sides of the container. When the molecules collide with the sides of the container, they exert a force which results in the pressure exerted by the gas. As the number of molecules of a gas increases, the more frequently they will collide with the sides of the container and the greater the pressure will be.
- 2. **The molecules themselves occupy negligible volume when compared to the volume occupied by the gas.** The volume of the gas consists of mainly empty space with tiny molecules randomly distributed with relatively large intermolecular distances.
- 3. **The average kinetic energy of the molecules is directly proportional to the absolute temperature of the gas.** The amount of kinetic energy the molecules possess will determine the speed of the molecules. Therefore as temperature increases, the kinetic energy of the molecules increases and the speed increases. This in turn increases the frequency of collisions of the molecules.
- 4. **Collisions are perfectly elastic.** When molecules collide, they bounce off each other with no loss of energy. This means that no attractive or repulsive forces are involved during collisions and the total energy of the molecules remains the same.
- 5. **The molecules exert no force on one another.** The molecules are not close enough for intermolecular forces of attraction to exist between them. The only interactions between molecules are their elastic collisions.





THE GAS LAWS

The gas laws are results of experiments explaining the responses of gases to changes in physical quantities. The gases are referred to as **ideal gases** when they obey the gas laws under all conditions.

Boyle's Law

Robert Boyle (1627-1691) investigated the relationship between the volume of a fixed mass of gas and its pressure at constant temperature. He found that when the pressure of the sample of gas was doubled, the volume was halved. The results of his work indicated that *the volume of a fixed mass of gas is inversely proportional to its pressure at constant temperature*. This is known as Boyle's law and can be expressed mathematically as

$$P \propto 1/V$$

$$P = k/V$$

where k is a constant

$$PV = \text{constant}$$

$$P_1 V_1 = P_2 V_2$$

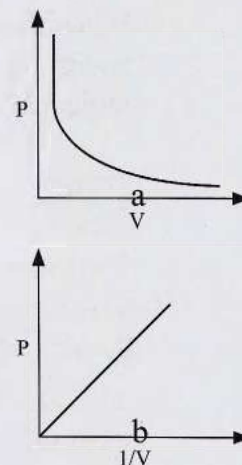


Fig. 5.1

Graphical representations of Boyle's law

Fig. 5.1

Charles' Law

Jacques Charles (1746-1823) and Joseph-Louis Gay-Lussac (1778-1850) made detailed measurements on how the volume of a gas was affected by changing the temperature. They showed that raising the temperature of a gas increased the volume of the gas if its pressure remained constant. Since Gay-Lussac made reference to Charles' unpublished work, the gas law is generally known as Charles' law which states that *the volume of a fixed mass of gas is directly proportional to its absolute temperature at constant pressure*. Mathematically this is represented as

$$V \propto T$$

$$V = kT$$

where k is a constant

$$V/T = \text{constant}$$

$$V_1/T_1 = V_2/T_2$$

When we plot a graph of volume of gas against temperature, we get a straight line.

Fig. 5.2

If we extend Charles Law to extremely low temperatures, the volume of the ideal gas should become zero. However, in reality a gas would change phase or liquefy long before it reaches zero

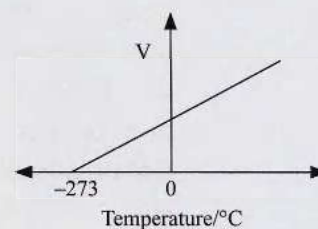


Fig. 5.2

A graphical representation of Charles' law



volume. The temperature at which the volume of a gas would become zero if it did not condense is called the **absolute zero** and can be found by extrapolating the graph to cut the temperature axis. When this is done, the temperature -273 is obtained for all gases. In 1848 Lord Kelvin used this as the basis for a new temperature scale called the **absolute temperature or the Kelvin (K)** which uses -273°C as the zero on the scale. On this scale, we can convert the degrees Celsius to Kelvins by adding 273. For example,

$$25^{\circ}\text{C} = 25 + 273 = 298\text{K}$$

Note it is important to use the Kelvin scale for calculations involving Charles' law.

The 'constant volume' law

When gases collide with the walls of their container they exert a pressure. The speed of the molecules and the number of collisions they make are affected by temperature. The relationship between the temperature and the pressure of a gas at constant volume is called the 'constant volume' law. It states that the pressure of a fixed mass of gas is directly proportional to the temperature at constant volume. Thus

$$\begin{aligned} P &\propto T \\ P &= kT \quad \text{where } k \text{ is a constant} \\ P/T &= \text{constant} \\ P_1/T_1 &= P_2/T_2 \end{aligned}$$

Ideal gas equation

Combining Boyle's law, Charles' law and the 'constant volume' law gives the equation

$$PV/T = \text{constant for a fixed mass of gas}$$

If we use one mole of gas, the constant is $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. This constant is called the **gas constant** and is given the symbol **R**. Thus for one mole of gas

$$PV/T = R$$

So for n moles of gas

$$PV/T = nR$$

or

$$PV = nRT$$

This is called the **ideal gas equation**. Units used in the ideal gas equation must be consistent. Thus the following units are used in



calculations involving the ideal gas equation:

P is measured in Pa

V is measured in m^3

T is measured in K

R is $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

The ideal gas equation can be used to find the relative molecular mass (M_r) of a gas.

Since

Number of moles of a gas (n) = mass of the gas (m) / M_r

Then

$$PV = mRT/M_r$$

Therefore

$$M_r = mRT/PV$$

Example 1

0.035 g of a gas was found to occupy a volume of 20 cm^3 at $1.09 \times 10^5 \text{ Pa}$ and 27°C . What is the relative molecular mass of the gas.

$$P = 1.09 \times 10^5 \text{ Pa}$$

$$V = 20 \text{ cm}^3 = 20 \times 10^{-6} \text{ m}^3$$

$$T = 27^\circ\text{C} = 273 + 27 = 300 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$m = 0.035 \text{ g}$$

Using the ideal gas equation

$$\begin{aligned} M_r &= mRT / PV \\ &= (0.035 \times 8.314 \times 300) / (1.09 \times 10^5 \times 20 \times 10^{-6}) \\ &= 39.86 \end{aligned}$$

The equilibrium state of a gas is specified by its temperature, pressure and volume. The gas laws can be combined into a single equation where the temperature, pressure and volume of a gas in one equilibrium state can be related to the corresponding properties in another. For example, if a gas has a volume V_1 , pressure P_1 and temperature T_1 in one system, then

$$P_1 V_1 / T_1 = nR$$



If the same gas occupies a new volume V_2 at pressure P_2 and temperature T_2 , then

$$P_2 V_2 / T_2 = nR$$

Thus

$$P_1 V_1 / T_1 = P_2 V_2 / T_2$$

This is called the **ideal gas equation of state**.

Example 2

A gas occupies 2 m^3 at 27°C and $1.01 \times 10^5 \text{ Pa}$. What volume will it occupy at 87°C and $4.04 \times 10^5 \text{ Pa}$.

$$P_1 = 1.01 \times 10^5 \text{ Pa}$$

$$P_2 = 4.04 \times 10^5 \text{ Pa}$$

$$V_1 = 2 \text{ m}^3$$

$$V_2 = ?$$

$$T_1 = 27^\circ\text{C} = 273 + 27 = 300 \text{ K}$$

$$T_2 = 87^\circ\text{C} = 360 \text{ K}$$

Using the equation

$$P_1 V_1 / T_1 = P_2 V_2 / T_2$$

$$\begin{aligned} V_2 &= (1.01 \times 10^5 \times 2 \times 360) / (300 \times 4.04 \times 10^5) \\ &= 0.6 \text{ m}^3 \end{aligned}$$



REAL & IDEAL GASES

When molecules of a gas behave independent of each other, the gas is termed as an ideal gas. The kinetic theory assumes that all gases are ideal and most discussions on gases assume that gases show ideal behaviour. On examining the behaviour of gases, these assumptions of the kinetic theory show that such a gas does not exist in reality. **However, under conditions of high temperatures and low pressures real gases approach ideal gas behaviour.**

Increase temperature of a gas increase the average kinetic energy of the gas molecules and cause them to speed up in their motion to one another. This increase in speed overcomes the intermolecular forces of attraction between the molecules and the gas behaves more like an ideal gas.

Decrease pressure allows the gas molecules to spread far apart from one another. As the molecules move further apart, the intermolecular forces of attraction approach zero and the gas behaves as an ideal gas.



Limitations of ideal gas behaviour

For ideal gases, it is assumed that a gas can be infinitely compressed or cooled and it will not liquefy. However, in reality if the gas is compressed or cooled enough it will deviate from ideal behaviour.

Real gases deviate from ideal gas behaviour at

- low temperatures
- high pressures i.e. $> 100 \text{ atm}$.

At low temperature the kinetic energy of the molecules decreases. This results in the collisions becoming less elastic and no longer being able to overcome the intermolecular forces of attraction between the molecules. So the assumption of the kinetic theory that there are no forces of attraction between the molecules no longer holds. Also the attractive forces of the molecules bring them close enough so that the volume of the gas becomes smaller, thus the assumption that the volume of the molecules is negligible when compared to the volume occupied by the gas becomes invalid.

As the temperature decreases below a critical value, the deviation from the ideal gas behaviour becomes severe because the molecules get close enough to form clusters of particles and condense to form a liquid which is held together by intermolecular forces of attraction.

At high pressure (100-200 atm) the molecules are pushed close together so that the intermolecular distance becomes shorter and attractive forces between the molecules become significant. Apart from reducing the volume occupied by the gas, the attractive forces reduce the momentum of the molecules as they bombard the walls of the container. This results in the pressure exerted by the gas being less than that for an ideal gas. Thus for one mole of gas $PV < RT$.

At very high pressure (200-1000 atm) the molecules are pushed so close together that they repel each other. The repulsive forces between the molecules increase the momentum of the molecules as they bombard the walls of the container so that the pressure exerted by the gas is greater than that for an ideal gas. Thus for one mole of gas $PV > RT$. At high pressures, the volume of the molecules becomes significant compared to the volume occupied by the gas and the gas shows non-ideal behaviour. Gases with

stronger intermolecular forces of attraction show greater deviation from ideal gases.

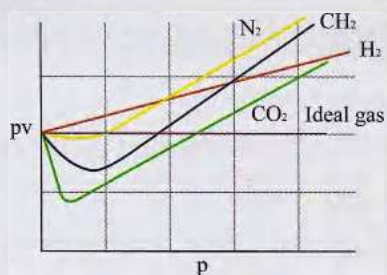
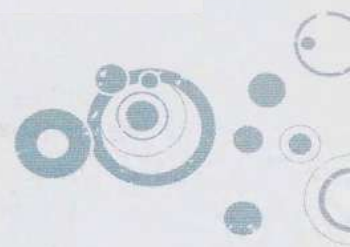
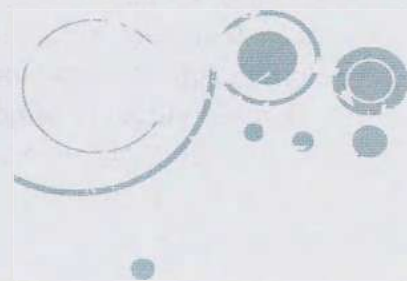
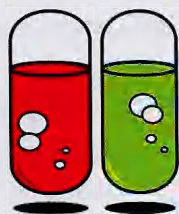


Fig. 5.3

Deviation of gases from ideal behaviour





Questions

1.
 - (a) List five assumptions of the kinetic theory.
 - (b) State Charles' law.
 - (c) Describe how the kinetic theory explains Charles' law.
 - (d) A mass of gas occupies 1000 cm^3 at a fixed pressure and a temperature of 25°C . What volume will the gas occupy at 35°C if it shows ideal behaviour.
2.
 - (a) What is meant by the term *ideal gas*?
 - (b) Under what conditions of temperature and pressure will a real gas deviate from ideal gas behaviour.
 - (c) What TWO assumptions of the kinetic theory of gases do not hold under the conditions described in (b) above.
 - (d) In an analysis, 0.1 g of a sample X occupied 25 cm^3 at 100°C and atmospheric pressure. Calculate the relative molecular mass of X.
3.
 - (a) Sketch the graph showing the relationship between the volume and temperature of a gas at a fixed pressure.
 - (b) Show on the graph the temperature at which the volume of an ideal gas becomes zero.
 - (c) 1.09 g of a gas occupied 920 cm^3 at 30°C and 93 kPa . Calculate the relative molecular mass of the gas.
4. Use the kinetic theory of matter to explain the following:
 - (a) the nature of the liquid state
 - (b) the change of state from liquid to gas
 - (c) gases have lower densities than liquids
5. A weather balloon containing 54 dm^3 of gas at 30°C and 2 atmospheres rises to an altitude where the temperature is 20°C and the pressure of the gas is 1 atmosphere.
 - (a) Calculate the change in volume of the gas in the balloon.
 - (b) Suggest a consequence of the change in volume of the gas.
 - (c) State an assumption made in your calculation.



Chemical reactions are usually accompanied by energy changes, principally in the form of heat energy. The energy within a system is referred to as the enthalpy and is denoted by the symbol H . Thus the energy change in a reaction is called the enthalpy change or ΔH .

The enthalpy change = energy of the products – energy of the reactants

$$\Delta H = H_p - H_R$$

Chemical reactions involve bond breaking followed by bond making. Bond breaking is endothermic while bond making is exothermic. Therefore all chemical reactions require a minimum amount of energy to break the bonds of reactant molecules before new bonds are formed to make the product. This energy is called the **activation energy (E_a)**. As reactant molecules absorb the activation energy, the bonds lengthen and weaken to form an activated complex or a transition state. In this complex the energy content is high and the complex is highly unstable. From the transition state two processes can occur, either the complex can decompose to the products or reform the reactants.



EXOTHERMIC REACTION

When the energy of the products is less than the energy of the reactants ΔH is negative and the reaction is **exothermic**. In exothermic reactions heat is given off from the reaction to the environment. If the reaction is conducted in a reaction vessel, the contents of the vessel get hotter as heat is released from the reaction to the surroundings in the reaction vessel.

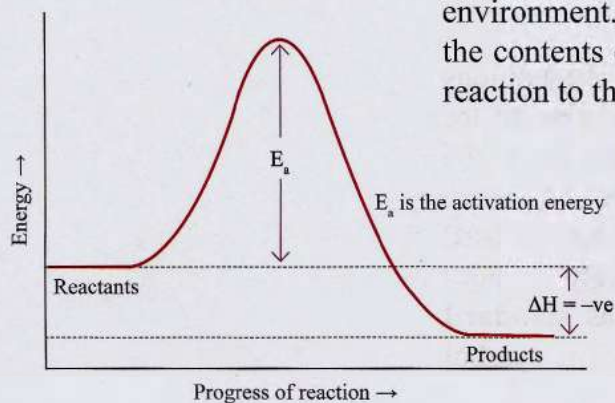


Fig. 6.1

Fig. 6.1

Energy profile diagram of an exothermic reaction



Fig. 6.1 shows the reactants gain the activation energy and increase in energy content forming the activated complex. The highly energetic complex can now decompose to form products or re-form the reactants. Reactions usually take place in order to form the most stable products. Since the products of this reaction have less energy than that of the reactant, the activated complex breaks down forming products. The products have less energy than the reactants thus ΔH is negative.



ENDOTHERMIC REACTION

When the energy of the products is greater than the energy of the reactants ΔH is positive and the reaction is **endothermic**. In endothermic reactions heat is absorbed from the surrounding into the reaction. If the reaction is conducted in a reaction vessel, the temperature within the vessel decreases as heat is absorbed from the contents of the reaction vessel.

► Fig. 6.2

In an endothermic reaction, the reactants gain the activation energy to form the activated complex. The complex then decomposes to form the products of the reaction. It can be seen in fig. 6.2 that in endothermic reactions the products have more energy than the reactants and are less stable. Most endothermic reactions do not take place readily. Appropriate conditions must be provided for these reactions to occur.

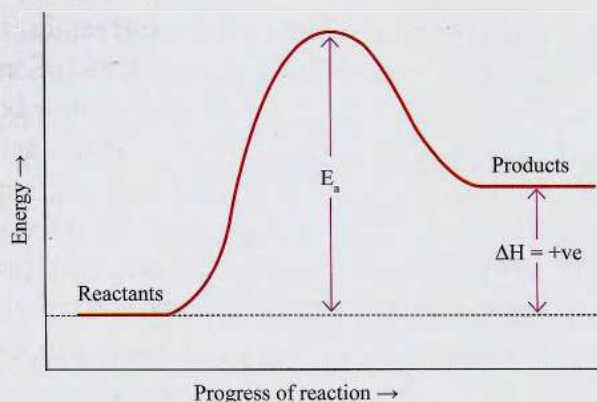


Fig. 6.2

Energy profile diagram of an endothermic reaction



STANDARD ENTHALPIES

Standard conditions for enthalpy measurements

To compare enthalpy changes it is important to state the conditions under which the reactions take place. The enthalpy change for a reaction depends on the amount of the substance used, the temperature and the pressure at which the reaction is performed. Standard conditions of 298K (25°C) and 1 atmosphere are used to measure and compare enthalpy changes. Enthalpy changes measured under these conditions are referred to as **standard enthalpy changes** and are given the symbol ΔH° . The symbol implies that

- all substances are in their normal physical state at 298K and 1 atmosphere



- enthalpy changes are measured per mole of the substance
- solutions involved have a concentration of 1 mol dm^{-3}

Therefore the standard enthalpy change of reaction (ΔH^{θ}_r) can be defined as the enthalpy change when the mole quantities shown in the balanced chemical equation react under standard conditions.

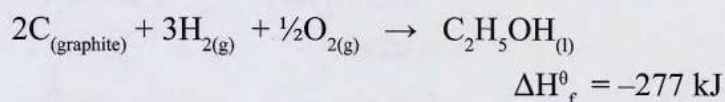
In cases where elements exist as different allotropes, the most stable form at 298K and 1 atmosphere is used as the standard. Thus the standard enthalpies for reactions involving carbon refer to graphite rather than diamond.

Standard enthalpy of formation (ΔH^{θ}_f)

The standard enthalpy of formation (ΔH^{θ}_f) is the heat change when one mole of substance is formed from its constituent elements in their normal states under standard conditions. Thus the enthalpy of formation of ethanol can be written as

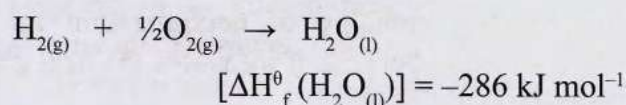
$$\Delta H^{\theta}_f [\text{C}_2\text{H}_5\text{OH}_{(l)}] = -277 \text{ kJ mol}^{-1}$$

This represents the equation

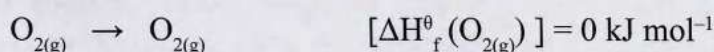


This means that 1 mole of ethanol is formed from 2 moles of carbon atoms, 3 moles of hydrogen molecules and $\frac{1}{2}$ mole of oxygen molecules.

Similarly, the equation for enthalpy of formation of water is given below.



It must be noted that the standard enthalpy of formation refers to the formation of only 1 mole of a compound and the equation for the reaction must be balanced to show the production of 1 mole of a substance. Hence only $\frac{1}{2}$ mole of oxygen molecules is required in the formation of water. Also the enthalpy change of an element in its normal physical state is zero and is used as the reference state of the element. No heat change is involved in the reaction as shown in the equation below.



Standard enthalpy of combustion (ΔH_c^θ)

The standard enthalpy of combustion (ΔH_c^θ) is the heat change when 1 mole of a substance is completely burnt in oxygen under standard conditions. The standard enthalpy of ethane is written as

$$\Delta H_c^\theta [\text{C}_2\text{H}_6(\text{g})] = -1560 \text{ kJ mol}^{-1}$$

This represents the equation



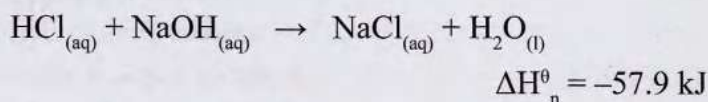
The substance must be completely burnt in oxygen to ensure 1 mole of the substance reacts.

Standard enthalpy of neutralization (ΔH_n^θ)

The standard enthalpy of neutralization (ΔH_n^θ) is the enthalpy change when an acid reacts with a base to form 1 mole of water under standard conditions. For example

$$\Delta H_n^\theta [\text{HCl} / \text{NaOH}_{(\text{aq})}] = -57.9 \text{ kJ mol}^{-1}$$

This represents the equation



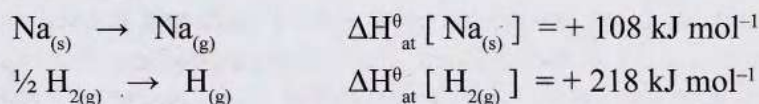
Although a balanced equation for the reaction between sulphuric acid and sodium hydroxide is



the standard enthalpy of neutralization for this reaction is $-57.9 \text{ kJ mol}^{-1}$ because it measures the heat change per mole of water formed.

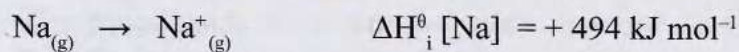
Standard enthalpy of atomization ($\Delta H_{\text{at}}^\theta$)

The standard enthalpy of atomization ($\Delta H_{\text{at}}^\theta$) is the heat change when 1 mole of gaseous atoms is formed from the element under standard conditions.



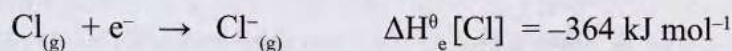
1st ionization energy

The 1st ionization energy is the enthalpy change when 1 mole of gaseous atoms is converted to gaseous ions with a single positive charge.



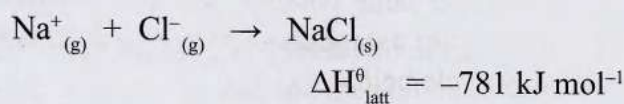
1st electron affinity

The 1st electron affinity is the enthalpy change when 1 mole of gaseous atoms is converted to gaseous ions with a single negative charge.



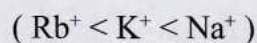
LATTICE ENERGY (ΔH^0_{latt})

The lattice energy (ΔH^0_{latt}) is the enthalpy change when 1 mole of an ionic solid is formed from its gaseous ions under standard conditions.

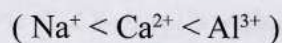


All lattice energies are negative since it involves forming bonds.

Lattice energy is a measure of the strength of the inter-ionic attraction. Consequently, the magnitude of the lattice energy increases as the size of the ion decreases and the charge of the ion increases. For example, the lattice energy of RbCl is less than that of KCl which is less than that of NaCl.



Similarly, the lattice energy of NaCl is less than that of CaCl_2 which is less than that of AlCl_3 .



Small, highly charged ions give the strongest electrostatic attraction.

Measuring enthalpy changes in the laboratory

A calorimeter is a piece of apparatus used in the laboratory to measure the enthalpy change for a reaction. The calorimeter is an insulated vessel in which the reaction takes place. Thus the temperature change in a reaction can be measured inside the calorimeter. The enthalpy change can then be calculated using the temperature change (ΔT) along with the mass (m) and specific heat capacity (c) of the contents in the calorimeter.

$$\text{Heat change} = mc\Delta T$$



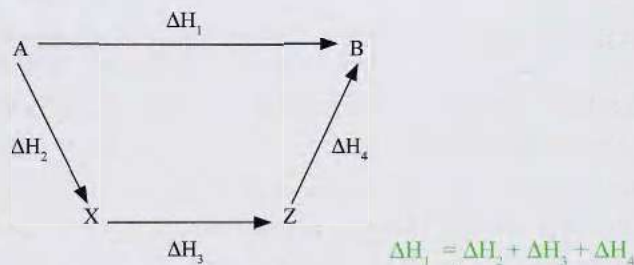
Like water, it is assumed that 1 cm^3 aqueous solutions = 1 g and the specific heat capacity of a dilute solution = $4.2 \text{ J K}^{-1} \text{ g}^{-1}$.



HESS'S LAW OF CONSTANT HEAT SUMMATION

In 1840, a Russian chemist named Germain Hess developed the thermochemical application of the law of conservation of energy known as Hess's law. *Hess's law states that the heat change in a reaction depends only on the nature of the reactants and products, no matter what reaction route is followed.* This means that the heat change in a reaction is the same whether the reaction takes place in one stage or through intermediate stages.

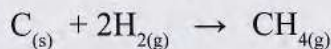
Consider the example below, the enthalpy change in the reaction A to B is the same whether the reaction proceeds in one stage $A \rightarrow B$ or in three stages $A \rightarrow X \rightarrow Z \rightarrow B$. This is represented in the enthalpy cycle below.



According to Hess, the enthalpy change in the reaction A to B is the same as the sum of enthalpy change for the reactions A to X, X to Z and Z to B.

Calculating the enthalpy change (ΔH) in a reaction

While calorimeters are effective in measuring the enthalpies of combustion and neutralization, some enthalpies cannot be measured directly. For example, in the formation of methane, carbon will not react with hydrogen under standard conditions in a calorimeter.



Although the standard enthalpy of formation of methane cannot be measured directly, it can be calculated indirectly by applying Hess's law or using bond energies.

Using Hess's law to calculate enthalpy changes

Hess's law can be used to determine the enthalpy of formation for methane indirectly from other known standard enthalpy changes

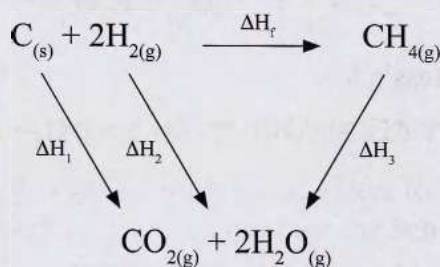


such as enthalpy of combustion. This is done by constructing an energy cycle diagram.

- First write the equation for the enthalpy change of formation of methane.



- Use given data to complete an energy cycle which may look like the one below.



- Applying Hess's law

$$\Delta H_f + \Delta H_3 = \Delta H_1 + \Delta H_2$$

clockwise arrows anti-clockwise arrows

Therefore

$$\Delta H_f = \Delta H_1 + \Delta H_2 - \Delta H_3$$

This means that the enthalpy of formation of methane is the same as the enthalpy of combustion for 1 mole of carbon plus the enthalpy of combustion for 2 moles of hydrogen molecules minus the enthalpy of combustion for 1 mole of methane. **A minus sign is used for ΔH_3 since the direction of the arrow is reversed.**

- Calculate the enthalpy of formation for methane using the following combustion data

$$\Delta H_c(\text{CH}_{4(g)}) = -890 \text{ kJ mol}^{-1}$$

$$\Delta H_c(\text{H}_{2(g)}) = -286 \text{ kJ mol}^{-1}$$

$$\Delta H_c(\text{C}_{(s)}) = -394 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta H_f &= (-394) + 2(-286) - (-890) \\ &= -76 \text{ kJ mol}^{-1} \end{aligned}$$

Examples

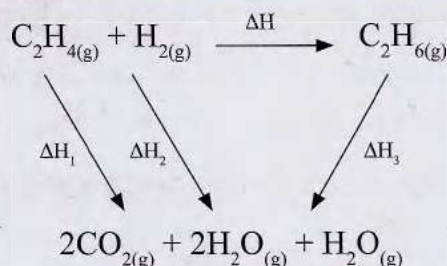
- Calculate ΔH for the hydrogenation of ethene given the following data:

$$\Delta H_c^\circ(\text{C}_2\text{H}_4) = -1411 \text{ kJ mol}^{-1}$$



$$\Delta H_c(\text{H}_2) = -286 \text{ kJ mol}^{-1}$$

$$\Delta H_c(\text{C}_2\text{H}_6) = -1560 \text{ kJ mol}^{-1}$$



Applying Hess's law

$$\Delta H + \Delta H_3 = \Delta H_1 + \Delta H_2$$

clockwise arrows anti-clockwise arrows

Therefore

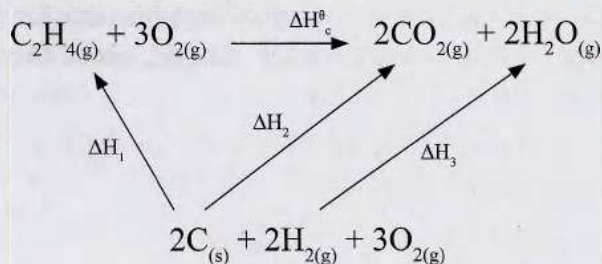
$$\begin{aligned} \Delta H &= \Delta H_1 + \Delta H_2 - \Delta H_3 \\ &= -1411 + (-286) - (-1560) \\ &= -137 \text{ kJ mol}^{-1} \end{aligned}$$

(ii) Calculate ΔH_c^θ of ethene given the following data:

$$\Delta H_f(\text{C}_2\text{H}_4) = 52 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{CO}_2) = -394 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{H}_2\text{O}) = -286 \text{ kJ mol}^{-1}$$



$$\begin{aligned} \Delta H_c^\theta &= -\Delta H_1 + \Delta H_2 + \Delta H_3 \\ &= -52 + 2(-394) + 2(-286) \\ &= -1412 \text{ kJ mol}^{-1} \end{aligned}$$

Using bond energies to calculate ΔH

Enthalpy changes can be calculated from bond energies. The bond energy is the energy absorbed when a bond is broken or the energy evolved when a bond is formed. The overall change in energy for bond breaking and bond forming is calculated as the enthalpy change for the reaction. For example, the enthalpy

of combustion of methane can be calculated from bond energy values as shown below.



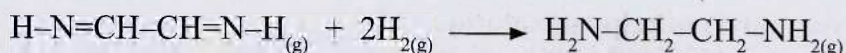
$$\begin{aligned}\text{Bonds broken} &= 4(\text{C}-\text{H}) + 2(\text{O}=\text{O}) \\ &= 4(+413) + 2(+498) \\ &= +2648\end{aligned}$$

$$\begin{aligned}\text{Bonds formed} &= 2(\text{C}=\text{O}) + 4(\text{O}-\text{H}) \\ &= 2(-805) + 4(-464) \\ &= -3466\end{aligned}$$

$$\begin{aligned}\Delta H_c^\theta &= +2648 - 3466 \\ &= -818 \text{ kJ mol}^{-1}\end{aligned}$$

Example

Calculate the enthalpy change for the following reaction using average bond energies.



$$\begin{aligned}\text{Bonds broken} &= 2(\text{H}-\text{H}) + 2(\text{C}=\text{N}) \\ &= 2(+436) + 2(+613) \\ &= +2098\end{aligned}$$

$$\begin{aligned}\text{Bonds formed} &= 2(\text{N}-\text{H}) + 2(\text{C}-\text{H}) + 2(\text{N}-\text{C}) \\ &= 2(-388) + 2(-412) + 2(-305) \\ &= -2210\end{aligned}$$

$$\begin{aligned}\Delta H_r^\theta &= +2098 - 2210 \\ &= -112 \text{ kJ mol}^{-1}\end{aligned}$$

Generally the values of enthalpies calculated from bond energies are similar to those that are determined experimentally. However, occasionally these values may differ from experimental values. This may be due to the environment of the bond in the molecule. For example a C-H bond in methane is in a different environment then the C-H bond in methanol.



ENTHALPY CHANGES IN SOLUTION

When an ionic solid dissolves in water two processes occur. Firstly the ions in the solid become separated from each other i.e. **the reverse of lattice energy**. This process is endothermic since bonds are broken. Secondly the separated ions become surrounded by water molecules. This process is called **hydration**



or **solvation**. It is an exothermic process since bonds are formed between the water molecules and the ions.

Standard enthalpy of hydration ($\Delta H^\circ_{\text{hyd}}$)

The standard enthalpy of hydration is the enthalpy change when one mole of gaseous ions is completely hydrated in water to infinite dilution under standard conditions.



The enthalpy of hydration for sodium chloride is the sum of the enthalpy of hydration of the cation and anion.



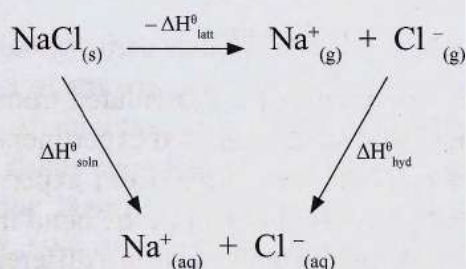
Therefore the enthalpy of hydration for sodium chloride is -783 kJ mol^{-1} .

Standard enthalpy of solution ($\Delta H^\circ_{\text{soln}}$)

Standard enthalpy of solution is the enthalpy change when 1 mole of a solute dissolves in a solvent to form an infinitely dilute solution under standard conditions.



The relationship between the enthalpy of solution, the lattice enthalpy and the enthalpy of hydration is shown in the energy cycle below.



Therefore

$$\Delta H^\circ_{\text{soln}} = -\Delta H^\circ_{\text{latt}} + \Delta H^\circ_{\text{hyd}}$$

It is the sum of the negative lattice enthalpy and the enthalpy of hydration of the ions in solution. Therefore the enthalpy of solution of sodium chloride is

$$\begin{aligned} \Delta H^\circ_{\text{soln}} (\text{NaCl}_{(\text{s})}) &= -(-787 \text{ kJ mol}^{-1}) + (-783 \text{ kJ mol}^{-1}) \\ &= +4 \text{ kJ mol}^{-1} \end{aligned}$$

The reverse of the lattice energy is always positive since it is an endothermic process which involves separating the ions in the ionic solid. On the other hand, the hydration energies for the ions are always negative since it is an exothermic process which involves forming bonds with water molecules. Thus the enthalpy of solution can be exothermic or endothermic depending on which of the process is larger. On dissolving solid sodium chloride, the energy required to break the lattice is more than the energy given off when the ions are hydrated therefore the overall reaction is endothermic.



BORN-HABER CYCLES

Max Born and Fritz Haber extended Hess's energy cycle to find enthalpy changes for ionic compounds. The energy cycle showing the formation of an ionic compound from its elements in a series of steps is called a Born-Haber cycle. The Born-Haber cycle for sodium chloride is shown in fig. 6.3 below.

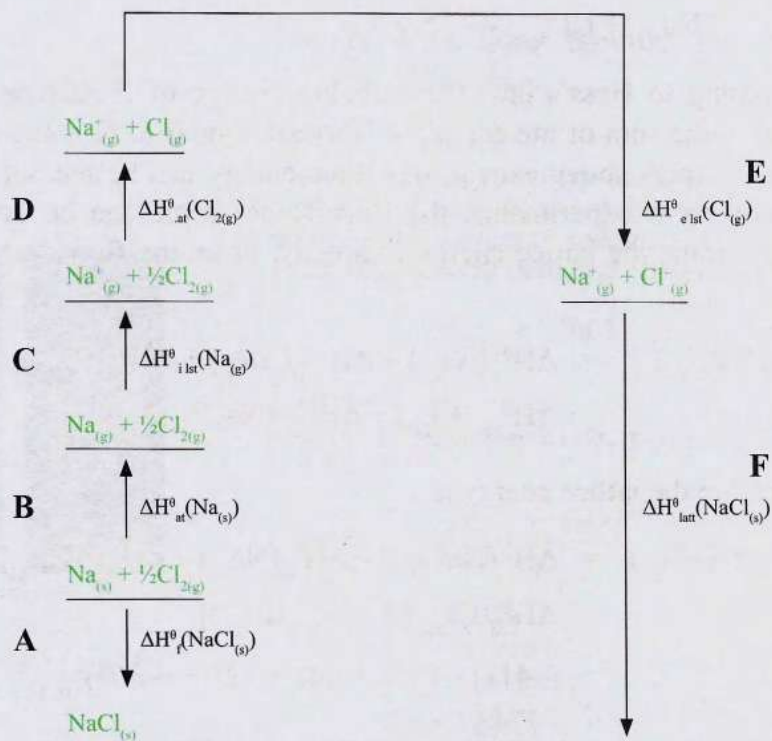


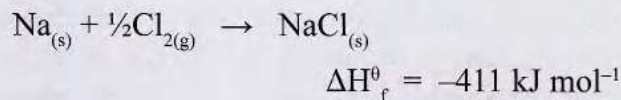
Fig. 6.3

The Born-Haber cycle of sodium chloride. Upward arrows represent endothermic reactions while downward arrows represent exothermic reactions.

Hess's law states that the enthalpy change for a reaction is independent of the pathway. Therefore the enthalpy of formation of sodium chloride is the same as the alternative pathway (B to F).



The direct path **A** for the formation of solid sodium chloride is given by the equation



The indirect path has five different steps (**B, C, D, E and F**).

- B is the atomization of solid sodium



- C is the 1st ionization of sodium atoms



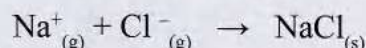
- D is the atomization of chlorine gas



- E is the 1st electron affinity of the chlorine atoms



- F is the lattice energy of sodium chloride



According to Hess's law, the enthalpy change of formation is equal to the sum of the enthalpies for reactions B to F. Since all the enthalpies above except the lattice energy can be measured directly from experiments, the Born-Haber cycle can be used to determine the lattice energy indirectly. From the Born-Haber cycle

$$\Delta H_f^\theta(\text{NaCl}_{(s)}) = \Delta H_{\text{at}}^\theta(\text{Na}_{(s)}) + \Delta H_{\text{1st}}^\theta(\text{Na}_{(g)}) + \Delta H_{\text{at}}^\theta(\text{Cl}_{2(g)}) + \Delta H_{\text{e1st}}^\theta(\text{Cl}_{(g)}) + \Delta H_{\text{latt}}^\theta(\text{NaCl}_{(s)})$$

Therefore the lattice energy is

$$\begin{aligned} \Delta H_{\text{latt}}^\theta(\text{NaCl}_{(s)}) &= \Delta H_f^\theta(\text{NaCl}_{(s)}) - [\Delta H_{\text{at}}^\theta(\text{Na}_{(s)}) + \Delta H_{\text{1st}}^\theta(\text{Na}_{(g)}) + \Delta H_{\text{at}}^\theta(\text{Cl}_{2(g)}) + \Delta H_{\text{e1st}}^\theta(\text{Cl}_{(g)})] \\ &= (-411) - [108 + 498 + 121 + (-364)] \\ &= -774 \text{ kJ mol}^{-1} \end{aligned}$$

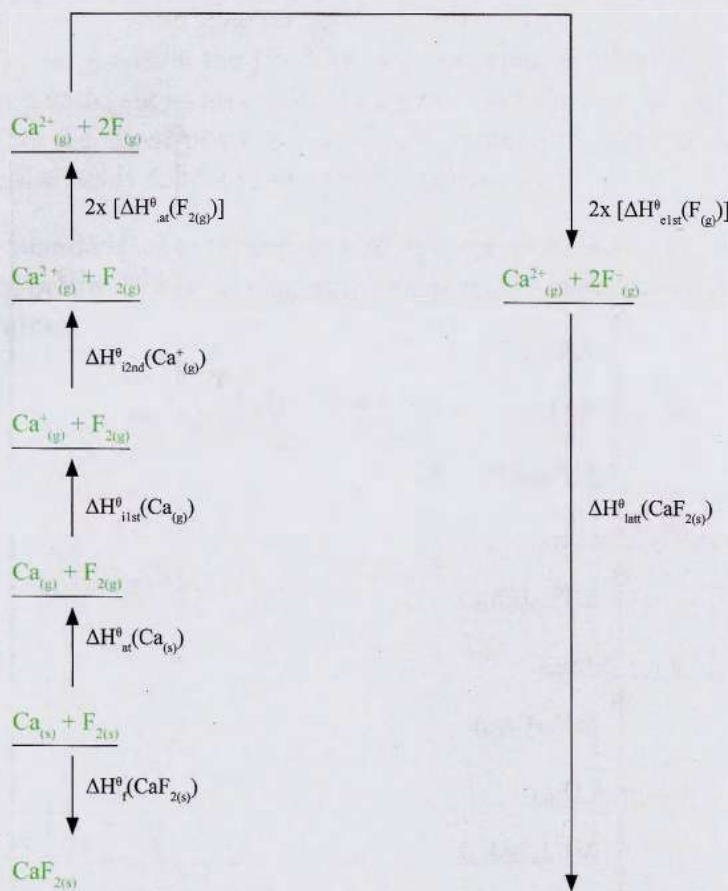


Fig. 6.4

The Born-Haber cycle of calcium fluoride. Upward arrows represent endothermic reactions while downward arrows represent exothermic reactions.

According to Hess's law

$$\Delta H_f^\circ(\text{CaF}_{2(s)}) = \Delta H_{\text{at}}^\circ(\text{Ca}_{(s)}) + \Delta H_{\text{i1st}}^\circ(\text{Ca}_{(g)}) + \Delta H_{\text{i2nd}}^\circ(\text{Ca}_{(g)}) + [2x \Delta H_{\text{at}}^\circ(\text{F}_{2(g)})] + [2x \Delta H_{\text{e1st}}^\circ(\text{F}_{(g)})] + \Delta H_{\text{latt}}^\circ(\text{CaF}_{2(s)})$$

Note that gaseous calcium is ionized twice to obtain the calcium cation with a +2 charge. Also twice the enthalpy of atomization is required to produce two moles of fluorine atoms and each mole of fluorine atom must gain electrons to produce two moles of negative anions for the reaction to occur.



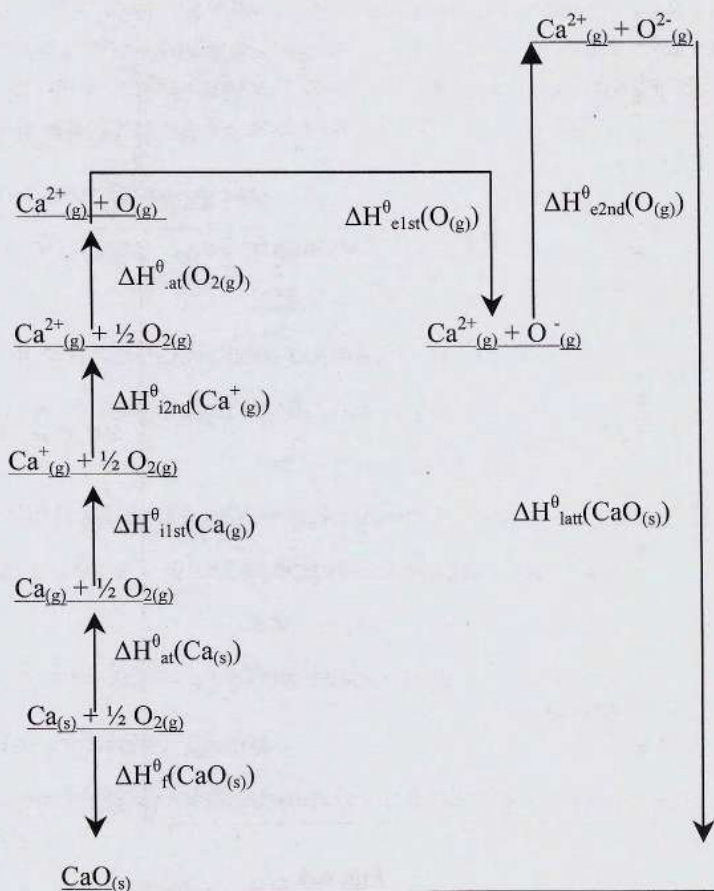


Fig. 6.5

The Born-Haber cycle of calcium oxide.



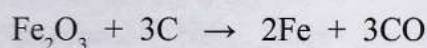
Questions

1. Define the following terms:
 - (a) Enthalpy change
 - (b) Enthalpy change of formation
 - (c) Enthalpy change of combustion
2. With the aid of energy profile diagrams and bond energies, explain the difference between an exothermic reaction and an endothermic reaction.
3. The enthalpy change for the formation of carbon monoxide cannot be obtained experimentally. Illustrate by means of an energy cycle diagram how the standard enthalpy of combustion of carbon and that of carbon monoxide can be used to obtain the standard enthalpy of formation for carbon monoxide.
4. What is the standard enthalpy change for the formation of liquid benzene given the following :

Substance	Standard heat of combustion/ kJ mol^{-1}
$\text{H}_2(\text{g})$	-286
$\text{C}(\text{s})$	-394
$\text{C}_6\text{H}_6(\text{l})$	-3350

5. Discuss the factors that affect the size of the lattice energy of a substance.
6. The enthalpy changes for two reactions are given below.
$$2\text{Fe} + 1\frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 \quad \Delta H = -822 \text{ kJ mol}^{-1}$$
$$\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} \quad \Delta H = -110 \text{ kJ mol}^{-1}$$

Calculate the enthalpy change for the following reaction:



7. (a) State Hess's law.
(b) Use the data below to draw the Born-Haber cycle for the formation of solid potassium chloride.
(c) Calculate the enthalpy change of formation of potassium chloride.

Enthalpy change of atomization of potassium
 $= +90 \text{ kJ mol}^{-1}$

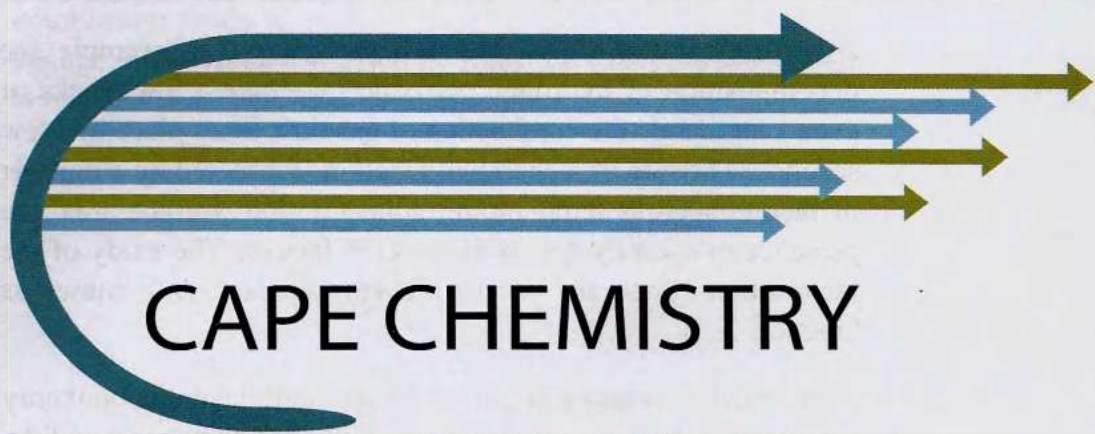
Enthalpy change of atomization of chlorine
 $= -121 \text{ kJ mol}^{-1}$

First ionization energy of potassium
 $= +418 \text{ kJ mol}^{-1}$

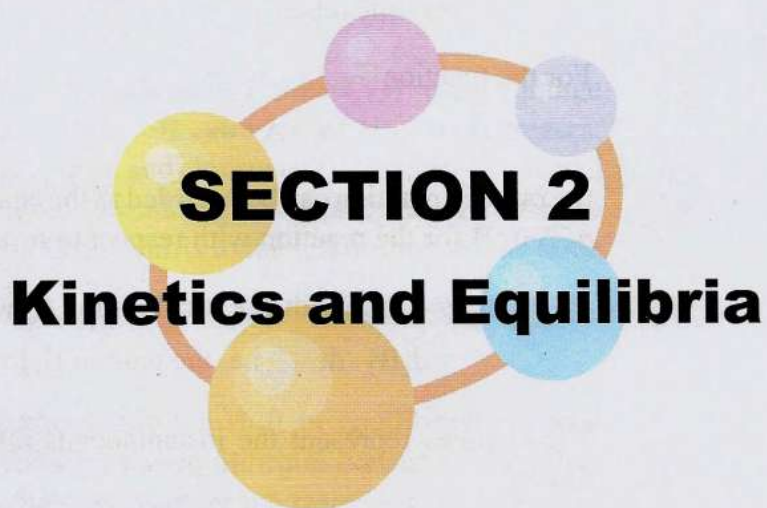
Electron affinity of chlorine
 $= -364 \text{ kJ mol}^{-1}$

Lattice energy of potassium chloride
 $= -701 \text{ kJ mol}^{-1}$

8. (a) Draw a Born-Haber cycle for the formation of aqueous potassium chloride.
(b) Given that the enthalpy of hydration of potassium ion is -322 kJ mol^{-1} and the enthalpy change of hydration of chloride ion is -364 kJ mol^{-1} , calculate the enthalpy change of solution of potassium chloride, using the lattice energy value in 7(c) above.
9. Explain the following observations as fully as you can:
(a) The enthalpy change for the neutralization of 1 mole of hydrochloric acid is -57 kJ mol^{-1} while that for the neutralization of sulphuric acid is -114 kJ mol^{-1} .
(b) The enthalpy change of solution of lithium chloride is negative while that of potassium chloride is positive.
10. The standard enthalpy changes of formation of carbon dioxide and water are -394 kJ mol^{-1} and -286 kJ mol^{-1} respectively. Calculate the enthalpy change of formation of propyne given its enthalpy change of combustion is $-1940 \text{ kJ mol}^{-1}$.



CAPE CHEMISTRY



Rates of Reactions

All chemical reactions have different rates for example the decomposition of hydrogen peroxide may take a few weeks or even years while the combustion of gasoline takes place in a few seconds. The rate of a chemical reaction is affected by a number of factors such as temperature, concentration, surface area, the presence of a catalyst as well as other factors. The study of the factors that affects the rate of a chemical reaction is known as kinetics.

For a reaction to take place we must consider the collision theory which states that for a reaction to occur the reactants must collide, the reactants must collide with sufficient energy to break bonds, and the molecules must collide with precise orientation for the reaction to occur.



THE RATE OF A CHEMICAL REACTION

The rate of a chemical reaction can be defined in two general ways:

- rate of consumption of a reactant (amount of reactant used per time taken)
- rate of formation of product (amount of product formed per time taken)

For the reaction



the rate of a reaction can be regarded as the change in concentration of A or B for the reaction with respect to time.

$$\begin{aligned} \text{Rate} &= -d[A]_t / dt \quad \text{i.e. the loss in } [A] \text{ with respect to time} \\ &= d[B]_t / dt \quad \text{i.e. the gain in } [B] \text{ with respect to time} \end{aligned}$$

The changes represent the instantaneous rate of the reaction at time t .

Concentrations are generally in mol dm^{-3} and time is in seconds. Thus the units for the rate of a reaction are $\text{mol dm}^{-3} \text{ s}^{-1}$.



The average rate of a reaction can be represented as

$$\frac{\text{amount of product formed}}{\text{time taken}}$$

Instantaneous rate measures rate for a particular time during the reaction whereas average rate measures the overall rate for the entire time period of the reaction.



METHODS OF MEASURING RATE

To measure the rate of a reaction, we must be able to measure the change in concentration of a reactant or a product with respect to time. In chemical reactions, any property that is proportional to concentration can be measured. Measuring different properties would require different techniques. For example, a reaction producing a gas requires a different technique to one that produces coloured liquid.

Finding the rate from a concentration versus time graph

To determine the rate of a reaction, changes in concentration at suitable time intervals must be obtained. A graph of concentration versus time is plotted. The rate of the reaction at time (z) is determined by drawing a tangent at time (z) and calculating the gradient at this point. The tangent at zero is called the initial rate which is the rate at the start of the reaction.

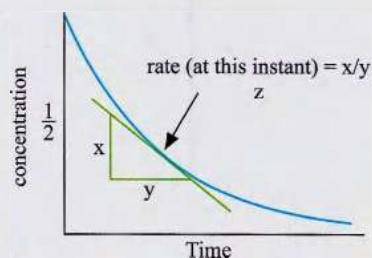


Fig. 7.1

Gradient calculated from concentration versus time graph

Fig. 7.1

Titration method

This is suitable for reactions in solutions. For example, the rate of hydrolysis of an ester can be measured using titration techniques.



A small sample known as an aliquot is pipetted at intervals during the course of the reaction and quenched. Quenching involves adding a reagent to the mixture to stop the reaction. The small portion that was pipetted will continue to react if it is not quenched.

The aim of quenching is to remove the kinetic energy so that the particles lack sufficient energy to react or to neutralize one of the reactant without affecting the other reactant so that it can be analyzed. Quick freezing is done by immersing the sample in an ice bath or a reagent such as sodium carbonate is added to quickly



Colorimetric method

- Standard solutions of iodine are placed in a spectrophotometer which records absorbance values.
- A standard calibration graph of absorbance versus concentration is plotted (normally gives a straight line).
- As the reaction starts, samples are withdrawn at measured time intervals and the absorbance is measured in the spectrophotometer.
- Using the standard calibration graph, interpolate to obtain the concentration of the sample.
- Data is therefore obtained in the form of concentration versus time for which a graph can be plotted and reaction rate can be determined by tangent.

Gas measurement method

If a gas is formed, its volume may be measured at suitable time intervals using a graduated gas syringe. If the gas is insoluble in water it may also be measured by the displacement of water from a measuring cylinder filled with water. The concentration of reactant at time (t) is proportional to the volume of gas at that time. As such, a graph of volume of gas versus time may then be plotted from which the rate of reaction can be calculated.

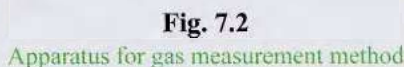


Fig. 7.2

Fig. 7.2



If the reaction is carried out at a constant volume and temperature, the change in pressure with time can be measured. This is done by attaching a manometer to the reaction flask.



RATE CONSTANT

Experiments show that there is a relationship between the rate of a reaction and the concentrations of individual reactants used in the reaction. This experimental relationship is known as the **rate law** or **rate equation** for the reaction.

For the reaction



the rate equation is

$$\text{Rate} = k[A]^n$$

where k is the **rate constant** and n is the **order of the reaction**. The brackets $[]$ represents concentration in mol dm^{-3} . In the rate equation, k is referred to as the constant of proportionality which is unique for each reaction. It has units which must be incorporated in the equation. As the concentration of A decreases, the rate decreases so that the rate constant remains constant.



THE ORDER OF A REACTION

The order of a reaction with respect to a particular reactant is the power to which the concentration of the reactant is raised in the experimentally determined rate equation. The overall order of a reaction is the sum of the individual orders as they appear in the rate equation. For example, in the reaction



the rate of the reaction is related to the concentration of the reactants by the rate equation

$$\text{Rate} = k[A]^x[B]^y$$

where k is the rate constant and x and y are the order with respect to the reactants A and B respectively. Usually x and y have values of 0, 1 and 2. The overall order of the reaction is $(x + y)$.

When the order is 0 (zero order), the concentration has no effect on the rate. When the order is 1 (first order), the rate doubles as the concentration doubles. When the order is 2 (second order), the rate quadruples as the concentration doubles.



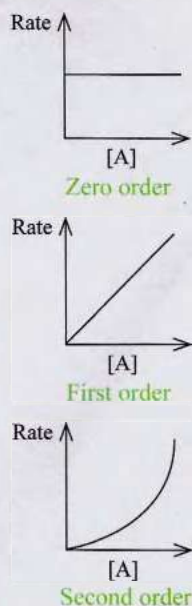


Fig. 7.3

The shapes of the rate-concentration graphs for a zero order, first order and second order reaction.

Determining the order of a reactant from concentration-time graph

Using experimental results, a concentration-time graph for reactant A can be plotted. The rate of the reaction can be determined by drawing tangents at different intervals on concentration-time graph. The rates at different times can then be used to plot a graph of rate versus concentration. The order of the reaction with respect to the reactant A can be determined from the shape of the rate-concentration graph. Fig. 7.3 shows the shapes of the rate-concentration graphs for a zero order, first order and second order reaction.

Fig. 7.3

Half-life method

The half-life of a reaction ($t_{1/2}$) is the time taken for the concentration of a reactant to fall to half its initial value. For first order reactions the half-life is constant. Therefore the first half-life ($t_{1/2}^{1st}$) of a reaction is equal to the second half-life ($t_{1/2}^{2nd}$) of the reaction. This means that it will take the same time for the concentration of the reactant to fall to half its initial value.

The half-life is related to the rate constant of a first order reaction by the expression

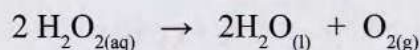
$$t_{1/2} = \ln 2 / k$$

thus if the half-life of a reactant is known then the rate constant of a first order reaction can be calculated using the relationship below.

$$k = 0.693 / t_{1/2}$$

Example 1

A dilute solution of H_2O_2 can be used to bleach hair. It decomposes slowly in aqueous solution.



A solution containing 3 mol dm^{-3} of H_2O_2 was placed in a bottle and contaminated with transition metal ions which act as a catalyst for the decomposition. The rate was measured by withdrawing 10 cm^3 portions at various times and titrating with acidified $0.1 \text{ mol dm}^{-3} \text{KMnO}_4$ (5 moles H_2O_2 react with 2 moles KMnO_4). The results are shown in the table 7.1

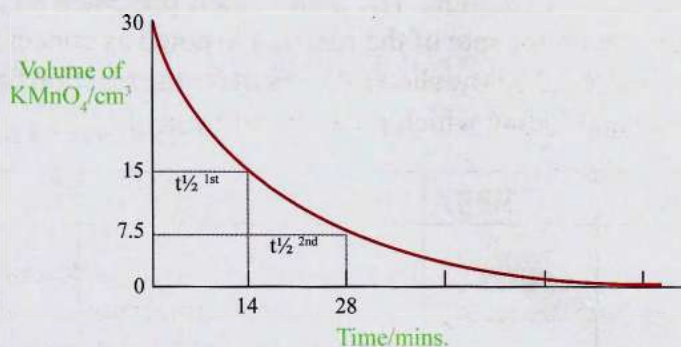
Time/min	Vol. of $0.1 \text{ mol dm}^{-3} \text{ KMnO}_4/\text{cm}^3$
0	30.0
5	23.4
10	18.3
15	14.2
20	11.1
25	8.7
30	6.8

Table 7.1

- Determine the order of the reaction with respect to the hydrogen peroxide.
- Write an expression for the rate equation and calculate the rate constant for the reaction.
- Calculate the concentration of the H_2O_2 at the time when the first portion was withdrawn. Hence estimate how long the solution had been in the contaminated bottle.
- Suggest a method whereby the half-life of the H_2O_2 solution can be increased.

Solution

- Since the concentration of acidified KMnO_4 is proportional to the H_2O_2 , plot a graph of volume of KMnO_4 used versus time. The first half-life of hydrogen peroxide would be equivalent to the time it takes for the KMnO_4 to change from 30 cm^3 to 15 cm^3 . The second half-life would be equivalent to the time it takes for the KMnO_4 to change from 15 cm^3 to 7.5 cm^3 .



$t_{1/2}^{1st} = 14 \text{ minutes}$

$t_{1/2}^{2nd} = 14 \text{ minutes}$

Therefore the reaction is first order with respect to H_2O_2 since the half-life is constant.





$$\text{Rate} = k [\text{H}_2\text{O}_2]$$

$$k = 0.693/t_{1/2}$$

$$= 0.693/14$$

$$= 4.95 \times 10^{-2}$$

(c) At zero minutes, the first portion was withdrawn.

30 cm³ of 0.1 mol dm⁻³ KMnO₄ contains 3×10^{-3} mole KMnO₄. Since 5 moles H₂O₂ reacts with 2 moles KMnO₄ then 7.5×10^{-3} mole H₂O₂ was present in 10 cm³ of solution therefore the concentration of H₂O₂ = 0.75 mol dm⁻³

If the concentration at zero minutes is 0.75 mol dm⁻³, then 14 minutes earlier it would have been 1.5 mol dm⁻³ and 14 minutes before that it would have been 3 mol dm⁻³. Therefore the solution would have been in the bottle 28 minutes before.

(d) The hydrogen peroxide can be placed in a dark bottle since light catalyzes its decomposition.

Initial rate method

This method is used for reactions that take long to occur. If the rate of a chemical reaction is quite slow then obtaining a useful set of measurements would take an inconvenient amount of time. However, we usually know the initial concentration of the reactants that we mix in the reaction flask and we can measure the initial rate of reaction. The data is then presented in a table and the effect on the rate of the reaction is noted as concentration changes. Table 7.2 below shows the result for the reaction between propanone and iodine which is catalyzed by acid.

Table 7.2

Experiment	[H ⁺]	[Propanone]	[Iodine]	Initial Rate
1	1.25	0.5	1.25	10.9
2	0.625	0.5	1.25	4.7
3	1.25	0.25	1.25	5.1
4	1.25	0.5	0.625	10.7

If we compare experiments 1 and 2 we will see the [H⁺] in 2 is half that in 1. The initial rate has also been approximately halved. From this data we can assume the reaction is first order with respect to the acid catalyst.

Also by observing 1 & 3 and 1 & 4 the reaction is first order with respect to propanone and zero order with respect to iodine.

Therefore the rate equation is

$$\text{Rate} = k [\text{H}^+] [\text{Propanone}] [\text{I}_2]^0 = k [\text{H}^+] [\text{Propanone}]$$

Thus the overall order of the reaction is 2 (second order).

We can also show this mathematically by taking the ratio of the rates from two experiments.

Comparing experiment 1 and 2 we can find the order with respect to $[\text{H}^+]$.

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{k [\text{H}^+]^a [\text{Propanone}]^b [\text{Iodine}]^c}{k [\text{H}^+]^a [\text{Propanone}]^b [\text{Iodine}]^c}$$

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{\cancel{k} [1.25]^a [0.5]^b [\cancel{1.25}]^c}{\cancel{k} [0.625]^a [\cancel{0.5}]^b [1.25]^c}$$

$$\frac{10.9}{4.7} = \frac{[1.25]^a}{[0.625]^a}$$

Rounding off to the nearest whole number

$$2 = 2^a$$

$$\text{Thus } a = 1$$

Similarly comparing experiment 1 and 3 where the $[\text{H}^+]$ and $[\text{Iodine}]$ remain constant we can find the order with respect to $[\text{Propanone}]$.

$$\frac{\text{Rate 1}}{\text{Rate 3}} = \frac{[\text{Propanone}]^b \text{ in expt. 1}}{[\text{Propanone}]^b \text{ in expt. 3}}$$

$$\frac{10.9}{5.1} = \frac{[0.5]^b}{[0.25]^b}$$

$$2 = 2^b$$

$$\text{Thus } b = 1$$



Also comparing experiment 1 and 4 where $[H^+]$ and $[Propanone]$ remain constant we can find the order with respect to $[Iodine]$.

$$\frac{\text{Rate 1}}{\text{Rate 4}} = \frac{[Iodine]^c \text{ in expt. 1}}{[Iodine]^c \text{ in expt. 4}}$$

$$\frac{10.9}{10.7} = \frac{[1.25]^c}{[0.625]^c}$$

$$1 = 2^c$$

$$\text{Thus } c = 0$$

Hence the rate equation is

$$\text{Rate} = k [H^+] [Propanone] [Iodine]^0 = k [H^+] [Propanone]$$

And the overall order of reaction is 2 (second order).



REACTION MECHANISMS

Once the rate equation is established, it is possible to suggest a mechanism of a reaction. The mechanism of a reaction shows all the steps and species that are involved in the reaction. A reaction usually has a slow stage which is called the rate determining step which is followed by one or more fast stages. The species that appear in the rate equation is involved in the rate determining step. Any other reacting species that does not appear in the rate equation are involved in the fast step, therefore by looking at the rate equation and the other species involved in the reaction one can propose a reaction mechanism that is consistent with the data.

Consider the reaction



$$\text{Rate} = k [A] [B]$$

This states that if the concentration of A is doubled then the rate is also doubled. This means that as the concentration of A doubles, there are twice as many particles of A to collide with B particles. Thus the rate increases proportionally. Similarly, doubling the concentration of B doubles the rate. The order is first order with respect to A and first order with respect to B. The overall order of the reaction is 2.

For the reaction



doubling the concentration of A implies that there are twice as many A particles to react. This means that twice as many A particles will collide with twice as many A neighbours. Thus as the concentration of A is doubled, the rate of production of B is quadruples. Therefore the reaction is second order. Generally for a simple one step reaction, the rate law can be predicted from the stoichiometric equation. For example,

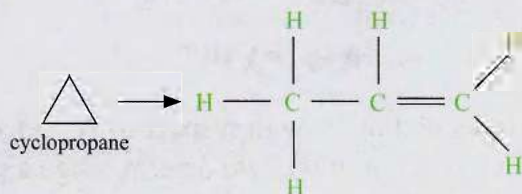


$$\text{Rate} = k [\text{H}_2] [\text{I}_2]$$

Both $[\text{H}_2]$ and $[\text{I}_2]$ directly affect the reaction rate. If either concentration is modified then the same modification is applied to the rate.

Molecularity

Molecularity refers to the number of reactant particles (atoms, molecules, radicals or ions) involved in a step of a reaction. When there is one reactant species involved in a reaction, the reaction is called a unimolecular reaction. For example



When there are two reactant species, the reaction is called a bimolecular reaction.



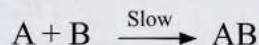
Reactions with a series of steps

Many chemical reactions are not simple one-step reactions but occur in a series of steps. Each step has its own activation energy. The slowest step in the reaction is the rate determining step.

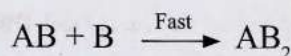
Consider the reaction



The steps for the reaction are



and



$$\text{Rate} = k [A] [B]$$

The coefficients of A and B in the rate determining step are the orders in the rate equation.

For the reaction



$$\text{Rate} = k [B]^2$$

This reaction is second order with respect to B. Since A is not in the rate equation, it is not in the rate determining step.

The rate determining step for this reaction may be

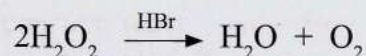


thus the fast step would be



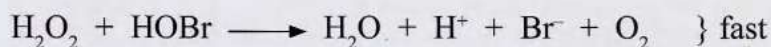
Consider the decomposition of H_2O_2 by HBr

The overall equation is



$$\text{Rate} = k [H_2O_2] [H^+] [Br^-]$$

The suggested steps for the reaction are



Catalysts have constant concentrations. The catalyst is the same before and after a reaction. Thus $[H^+][Br^-]$ is a constant, so the rate equation can be modified as follows:

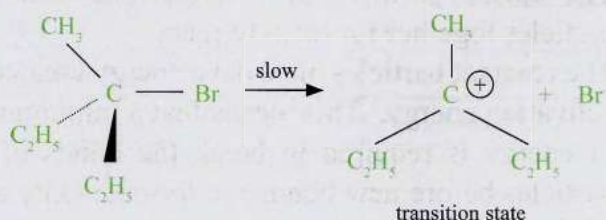
$$\text{Rate} = K' [H_2O_2] \quad \text{where } K' \text{ is a constant}$$

This is called a pseudo-first order reaction.

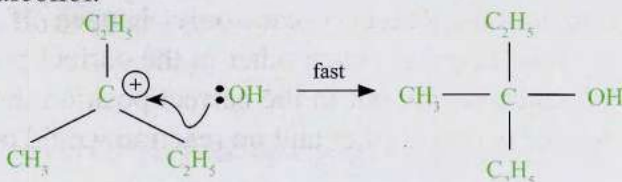
Consider the hydrolysis of a tertiary halogenoalkane with rate equation

$$\text{Rate} = k [\text{halogenoalkane}]$$

The mechanism proposed for the hydrolysis of a tertiary halogenoalkane e.g. 3-bromo-3-methylpentane involves the dissociation of the halogenoalkane into a carbocation and a halide ion.



Then the carbocation quickly reacts with the hydroxide ion to form an alcohol.



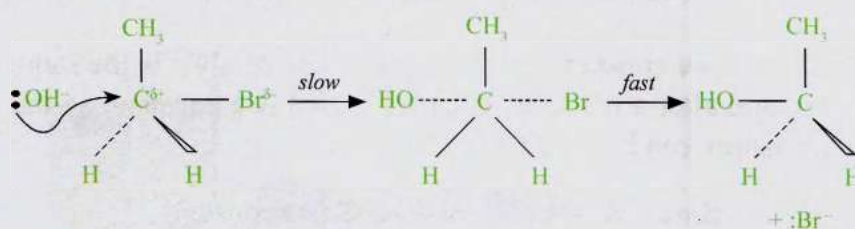
Since one species is involved in the formation of the transition state, the reaction is unimolecular. The breakage of the C-Br bond in the reactant is the rate determining step. This bond is relatively strong and takes longer to break requiring more energy.

The mechanism proposed for the hydrolysis of a primary halogenoalkane e.g. bromoethane with a rate equation

$$\text{Rate} = k [\text{halogenoalkane}] [OH^-]$$

involves bond breakage and bond formation at the same time. A transition state is reached where C is bonded to both O and Br. The transition state is then quickly converted into products.





Since two species are involved in the formation of the transition state, the reaction is bimolecular. This means the rate determining step also involves the OH^- ion.



COLLISION THEORY

Collision theory explains how chemical reactions occur and why reaction rates differ for different reactions. It postulates the following for a reaction to occur:

- The reactant particles must collide. Collisions bring the particles together for them to react.
- The reactant particles must have energy greater than the activation energy. This means that a minimum amount of energy is required to break the bonds of reactant particles before new bonds are formed. Only a fraction of the reactant particles have energy greater than the activation energy.
- The reactant particles must collide in the correct orientation. Reaction can only happen if reactant particles approach each other in the correct position. If the reactants are not in the correct position they would bounce off each other and no reaction would occur.

Not all molecules that collide react. Only effective collisions cause the transformation of reactants into products. This is because only a fraction of the molecules have sufficient energy and the right orientation at the moment of impact to break the existing bonds and form new bonds. The rate of a reaction may thus be defined as the number of effective collisions per unit time.



FACTORS AFFECTING RATE

Concentration

According to the collision theory, increase in concentration of reactants increases the frequency of collision between the reactants. Thus the effective collision frequency also increases. Therefore an increase in concentration of the reactants increases the rate of a reaction.

Particle size

In heterogeneous reactions, the greater surface area exposed to reactant particles, the more collisions can occur. Finely divided solids give a larger surface area and hence a faster rate of reaction than larger solids.

Temperature

An increase in temperature increases the kinetic energy of the reactant particles. This increases the number of collisions and also the fraction of particles having kinetic energy higher than the activation energy. Thus the effective collision frequency increases. Therefore an increase in temperature of the reactants increases the rate of a reaction.

Maxwell and Boltzmann calculated the distribution of velocities amongst molecules of gases using the laws of probability. The kinetic energy of molecules is shown in the graphical representation of the Maxwell-Boltzmann distribution in fig. 7.4.

Fig. 7.4

The curve in fig. 7.4 gives a representation of how energies are distributed in the reactant particles at a particular temperature. The shaded area under the curve shows the number of reactant molecules with energy greater than the activation energy at that temperature. The bulk of the molecules have energies below the activation energy.

As the temperature increases, the number of molecules with energies equal to or greater than the activation energy increases. Thus the shape of the curve flattens out and shifts to the right as shown in fig. 7.5. It is noticed that with an increase of 10°C the number of molecules with energies greater than the activation energy doubles. Thus an increase of 10°C roughly doubles the rate of a chemical reaction.

Fig. 7.5

Catalyst

A catalyst is defined as a substance which increases the rate of a chemical reaction but remains unchanged at the end of the reaction. The catalyst may be consumed in the reaction but it is regenerated at the end of the reaction. A catalyst speeds up the rate of a chemical reaction by lowering the activation energy (E_a). It provides an alternative pathway with lower E_a for the reaction to occur.

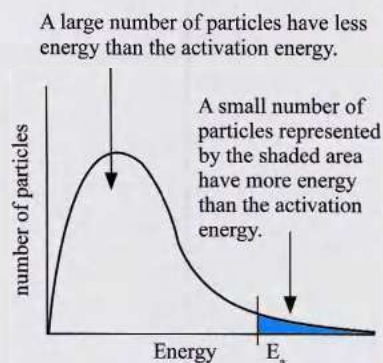


Fig. 7.4

The Maxwell-Boltzmann Distribution shows the number of particles that possess a particular energy.

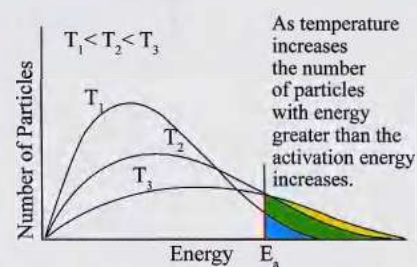


Fig. 7.5

The shape of the Maxwell-Boltzmann Distribution changes as temperature changes.



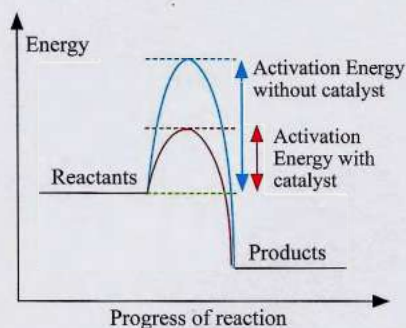


Fig. 7.6

Energy profile diagram for catalyzed and uncatalyzed reactions

Adding a catalyst provides an alternative route for the reaction. That alternative route has lower activation energy. This is shown on the energy profile diagram in fig. 7.6.

Fig. 7.6

Catalysts are divided into 2 groups. These are

- **synthetic catalysts**
- **biological catalysts** (these are known as enzymes which are proteins and are found in all living organisms)

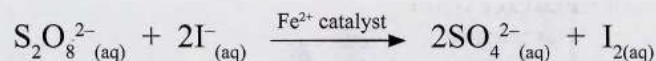
Synthetic catalysts are further divided into two groups. These are

- **Homogeneous catalysts** - the catalyst and the reactants are in the same physical state.
- **Heterogeneous catalysts** - the reactants and the catalyst are in a different physical state. e.g. V_2O_5 in the Contact process and Fe in the Haber process.

Homogeneous catalysts

Homogeneous catalysts are catalysts that are in the same state as the reactants. They are predominantly catalysts in solution along with reactants. Since they are dispersed within a solution, the surface area of the catalyst is maximized. A common example is H^+ ions which catalyzes a number of organic reactions such as the esterification reaction between a carboxylic acid and an alcohol, and the hydrolysis of sucrose to produce glucose and fructose.

Homogeneous catalysts provide an alternative pathway with lower activation energy for the reaction. The reaction between peroxodisulphate (VI) ions and iodide ions is given below. It is catalyzed by Fe^{2+} ions.



Although peroxodisulphate (VI) ions are very powerful oxidizing agents and iodide ions are very easily oxidized to iodine, the reaction between them in aqueous solution is very slow. This is because there is collision between two negative ions hence repulsion slows down the reaction. However adding Fe^{2+} ions increases the rate.

It is suggested that the catalyzed reaction takes place via two steps. First the peroxodisulphate (VI) ions oxidize the Fe^{2+} ions to Fe^{3+} ions.



Then the Fe^{3+} ions oxidize the iodide ions to iodine, regenerating the Fe^{2+} catalyst.



The suggested energy profile diagram for the reaction is shown in fig. 7.7. It shows the activation energy of the uncatalyzed reaction (E_{a3}) is higher than the activation energy of the two steps of the catalyzed reaction (E_{a1} and E_{a2}).

Fig. 7.7

The catalyst results in collision between positive and negative ions. These would be more successful than collision between two negative ions in the uncatalyzed reaction.

Heterogeneous catalysts

Typical examples involve a solid catalyst with the reactants as either liquids or gases. Gases that are reacting on metal surfaces such as transition metals in which the transition metals are acting as catalysts provide suitable examples of heterogeneous catalysts. Transition metals are frequently used as catalysts as they have unfilled d orbitals which can be used to form bonds.

Most examples of heterogeneous catalysis go through the same stages. First the reactants are adsorbed on to the surface of the catalyst at active sites. **Adsorption** is the temporary attraction of molecules of a gas or liquid to a solid surface. The reaction may be catalyzed in either or both of the following ways.

- When the reactant molecules are adsorbed onto the metal, the bonds within the reactant molecules weaken as some of its electrons are used to form bonds with the metal. This allows the reaction to take place more readily as the energy for bond breaking is less.
- The reactant adsorbed onto the metal may be held in the correct orientation for a reaction to occur. This increases the number of favourable collisions and hence increases the rate of the reaction.

The overall effect is to lower the activation energy. The product

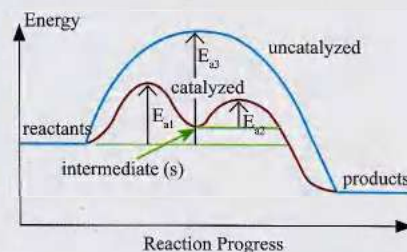


Fig. 7.7

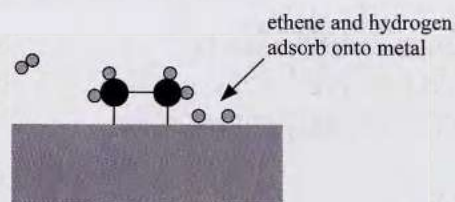
The activation energy of the uncatalyzed reaction is higher than the activation energy of the two steps of the catalyzed reaction.



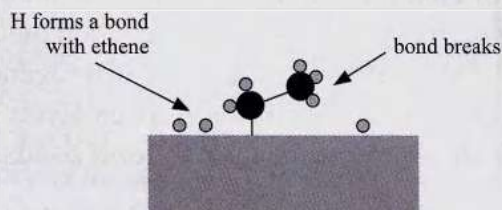
molecules then break away from the metal surface leaving the active sites available for a new set of molecules to attach to and react. A good catalyst needs to adsorb the reactant molecules strongly enough for them to react, but not too strong so that the product molecules cannot break away. If the product cannot break away from the surface of the metal, it blocks the active sites and prevents further reaction. Impurities in the reaction mixture usually adsorb more strongly than the reactants and block the active sites. The catalyst is then said to be poisoned.

The catalyzed reaction for hydrogenation of a carbon-carbon double bond in ethene is shown below.

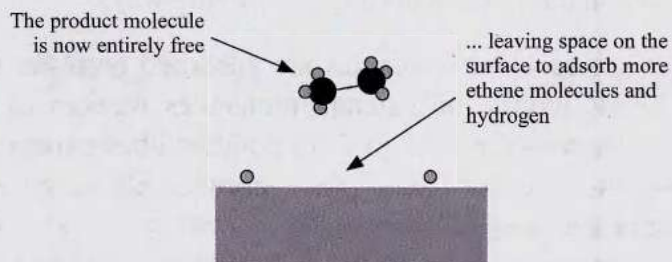
Hydrogen and ethene adsorb onto the metal surface. The double bond between the carbon atoms breaks and the electrons are used to bond it to the metal surface.



The bond between the carbon and hydrogen is formed.



The ethene molecule breaks free leaving space on the surface of the metal for new reactant molecules to go through the same process.



Hydrogenation of vegetable oils to make margarine involves reacting a carbon-carbon double bond in the vegetable oil with hydrogen in the presence of a nickel catalyst.

Catalytic converters use heterogenous catalysts. They change harmful molecules like carbon monoxide and various nitrogen oxides in car exhausts into less harmful molecules like carbon dioxide and nitrogen. They use transition metals like platinum, palladium and rhodium as the heterogeneous catalyst. The metals are expensive thus they are deposited as thin layers onto a ceramic honeycomb. This maximizes the surface area and keeps the amount of metal used to a minimum.

The catalyst works in the same way as above. The carbon monoxide and nitrogen monoxide adsorbed on the surface of the catalyst where they react. Then the product molecules break away from the metal catalyst.

Table 7.3

Some common reactions using catalysts:

Reactions	Catalysts
Decomposition of hydrogen peroxide	Manganese(IV) oxide, MnO_2
Ammonia by the Haber Process	Iron, Fe
SO_2 into SO_3 in the Contact Process	Vanadium(V) oxide, V_2O_5
Hydrogenation of a C=C double bond	Nickel, Ni

On the Maxwell-Boltzmann distribution shown in fig. 7.8 only those particles in the shaded area have energies higher than the activation energy and can react when they collide. The other molecules do not have enough energy to react.

Fig. 7.8

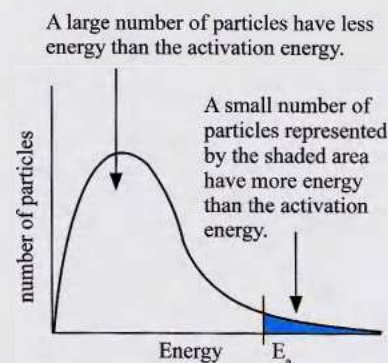


Fig. 7.8

Particles in the shaded area have energies higher than the activation energy in the Maxwell-Boltzmann distribution

A catalyst lowers the activation energy for the reaction. Therefore with lower activation energy, a greater number of molecules would have energy greater than the non-catalyzed activation energy. This is shown in the distribution curve in fig. 7.9.

Fig. 7.9

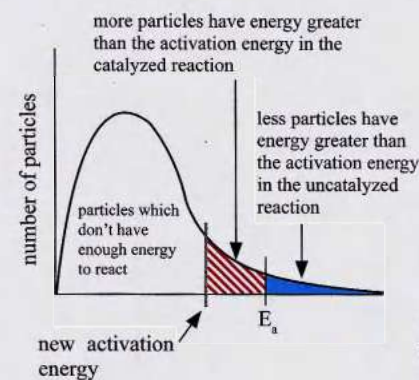


Fig. 7.9

More particles have energy higher than the activation energy in the Maxwell-Boltzmann distribution





Questions

1. The rate of the reaction between nitrogen monoxide and oxygen is given below.

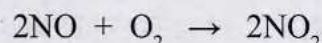
$$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$$

Predict quantitatively what would happen to the rate of the reaction when the following changes are made:

- (a) The concentration of O_2 is halved.
- (b) The concentration of NO is doubled.
- (c) The concentration of O_2 and NO are both tripled.

Explain your answer in each case.

2. The equation for the reaction between nitrogen monoxide and oxygen is given below.



- (a) Suggest a method of monitoring the rate of this reaction
- (b) Suggest a precaution that should be taken when performing the experiment.

Four experiments were carried out to find the relationship between the initial concentration of NO and O_2 , and the initial rate of formation of NO_2 .

experiment	Initial conc. of $\text{NO}/\text{mol dm}^{-3}$	Initial conc. of $\text{O}_2/\text{mol dm}^{-3}$	Rate of formation of $\text{NO}_2/\text{mol dm}^{-3}\text{s}^{-1}$
1	0.001	0.001	6×10^{-6}
2	0.001	0.002	12×10^{-6}
3	0.001	0.003	18×10^{-6}
4	0.002	0.003	72×10^{-6}

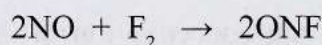
- (c) What is the order of the reaction with respect to each of the reactants?
- (d) What is the overall order of the reaction?
- (e) Write the rate equation for the reaction.
- (f) Calculate a value for the rate constant.



3. Use the collision theory to explain how the following factors affect the rate of a chemical reaction:
 - (a) Temperature
 - (b) Concentration
 - (c) Particle size
 - (d) Catalyst
4. Using the Maxwell-Boltzmann distribution of energy, explain the effect of temperature and a catalyst on the rate of a reaction.
5. The table below gives the results of an experiment to investigate the decomposition of compound X.

[X]/mol dm ⁻³	5.0	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5
Time/s	0	10	21	36	50	70	91	120	160	230

- (a) Explain the meaning of the following:
 - (i) rate of reaction
 - (ii) order of reaction
 - (b)
 - (i) Plot a graph of the concentration of X against time.
 - (ii) Determine the concentration of X after 75 seconds.
 - (iii) Describe how the graph plotted can be used to construct a graph of rate against concentration.
 - (c) Define the term half-life of a reaction.
 - (d) Using the graph in (b) (i) and the half-life method, determine the order of the reaction for the decomposition of X.
 - (e) Deduce the rate equation and hence calculate the rate constant.
6. The compound nitrosyl fluoride (ONF) is produced from nitrogen monoxide and fluorine according to the equation below.



The rate equation for the reaction is

$$\text{Rate} = k [\text{NO}] [\text{F}_2]$$

Suggest a mechanism for the reaction.





DYNAMIC EQUILIBRIUM

When solid iodine is placed in a glass tank and covered at temperature T , sublimation of the solid occurs. Gaseous iodine is purple in colour and as sublimation occurs the intensity of the purple vapour gradually increases until it stays constant. At this point the solid iodine has reached equilibrium with the iodine vapour.

At the macroscopic level it would seem that there is no movement occurring. The concentration of the iodine vapour as well as the concentration of solid iodine remains constant once equilibrium has been achieved. At the microscopic level there is movement in the system. The iodine vapour is being converted to solid iodine at the same rate the solid is being converted into the vapour. We say that the system is in a state of **dynamic equilibrium** when the rate of the reverse reaction is equal to the rate of the forward reaction. It should be noted that the tank was covered to create a closed system. A closed system is one in which no substances are either added to or lost from the system. In this system the reaction is isolated from external changes. For example, an equilibrium reaction involving gases must be sealed to prevent loss of gases which will affect concentration.

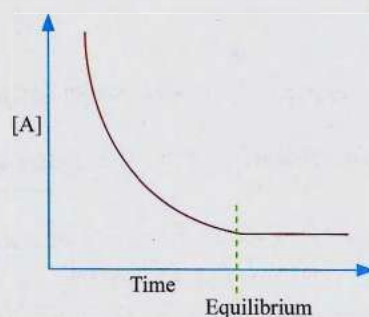
Dynamic equilibrium implies that movement persists within the system. Consider the following reaction:



In this reaction the concentration of A would decrease as the reaction proceeds until it reaches equilibrium. The concentration of A remains constant when equilibrium has been achieved. This can be represented graphically as shown in Fig. 8.1.

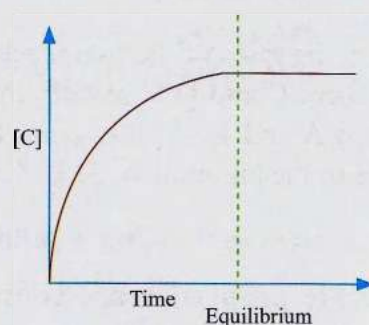


Fig. 8.1



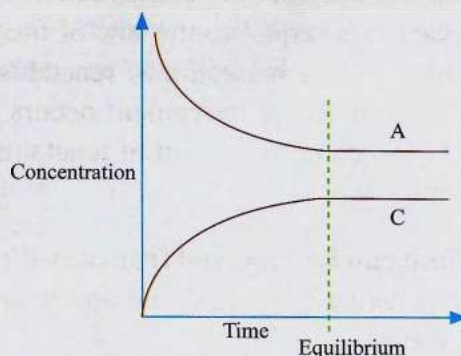
If we monitor the concentration of C, we will notice that the concentration of C increases as the reaction proceeds until it reaches equilibrium. At equilibrium, the concentration of C remains constant. This can be represented graphically as shown in Fig. 8.2

Fig. 8.2



At equilibrium, the concentration of A and C remains constant. Combining the two graphs above gives the graph below.

Fig. 8.3



Since the reaction is in dynamic equilibrium, A and B combine to produce C and D while C and D combine to produce A and B. At equilibrium, the rate of conversion of A and B to produce C and D is equal to the rate of conversion of C and D to produce A and B. The concentration of both the reactants and products will remain constant and neither of their concentration ever falls to zero.

If the rates of the forward and reverse reaction are plotted against time the graph in Fig. 8.4 is obtained.

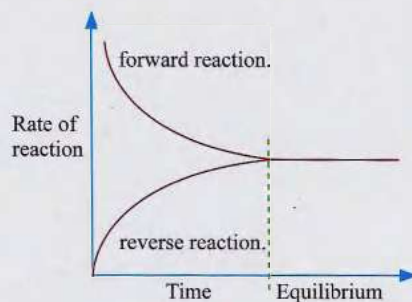


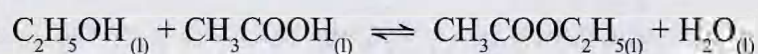
Fig. 8.4

The rate of the forward reaction falls with time as A and B are used to form C and D. At the start of the reaction there is no C and D, but as A and B form C and D, their concentrations increase. As the concentration of C and D increases, the rate of the reaction between C and D increases.

At equilibrium, the rates of the two reactions will become equal. A and B will form C and D at exactly the same rate as C and D convert back to A and B. At this point there would not be any further change in the amounts of A, B, C and D in the mixture.

Features of a system in dynamic equilibrium

- **Macroscopic properties are constant.** At equilibrium it appears that no reaction is occurring as no movement is observed, that is no visible reaction is taking place.
- **Microscopic properties are continuous.** Since the rate of the forward reaction is equal to the rate of the reverse reaction, there is continuous conversion of reactants to products and vice versa. Microscopic movement occurs however there is no change on the concentration of reactants and products at equilibrium.
- **Equilibrium can be achieved from any direction.** Consider the reaction between an acid and an alcohol to produce an ester and water.



To achieve equilibrium we can mix the alcohol and the acid or we can combine the ester with water. Whichever direction we choose to start from, equilibrium will be achieved.

- **Equilibrium can only be achieved if the system is closed.** This refers to a system in which there is no external interference. No substances are either added to or lost from the system.

- If the system is subjected to a disturbance e.g. a change in concentration or temperature, it responds to minimize the effect of the disturbance and returns to equilibrium over a finite period of time.



THE EQUILIBRIUM CONSTANT K_c

In dynamic equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction as mentioned earlier. Consider the reaction



If we assume that increasing the concentration of A or B will proportionally increase the concentration of products, then the rate is proportional to the concentration of A and B.

This can be expressed mathematically as

$$\text{Rate} = k_1 [A][B]$$

where the brackets [] represents concentration in mol dm^{-3}
 k_1 is the proportionality constant.

The rate of the reverse reaction will therefore be

$$\text{Rate} = k_2 [C][D]$$

At equilibrium the rate of forward reaction is equal to the rate of the reverse reaction.

Therefore $k_1[A][B] = k_2[C][D]$

This can be rewritten as

$$k_1 / k_2 = [C][D] / [A][B]$$

The constant k_1 divided by a constant k_2 gives a new constant K_c . Since we are using concentration of reactants and products, a subscript c is used to highlight this. Thus the equation can be written as

$$K_c = [C][D] / [A][B]$$

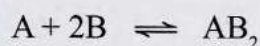
K_c is called the equilibrium constant and is written as the ratio of the concentration of the products and reactants. Generally the ratio is related to the stoichiometry of the reaction. For example



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The power to which the concentration of a substance is raised in the equilibrium expression is the same as its coefficient in the stoichiometric equation. In this equation a, b, c, and d are the respective coefficients of the substances A, B, C and D in the stoichiometric equation. This relationship between the equilibrium constant and the stoichiometric equation is known as the **equilibrium law**.

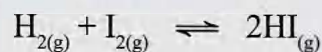
Consider the following



$$K_c = \frac{[AB_2]}{[A][B]^2}$$

Note that the numerator is the product and the denominator is the reactants.

Consider the reaction



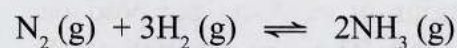
$$K_c = \frac{[HI_{(g)}]^2}{[H_{2(g)}][I_{2(g)}]}$$

Since the concentration is in mol dm^{-3} , the units for K_c must also be determined. For the reaction above, the units for K_c can be found by including it in the equilibrium equation.

$$K_c = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}$$

In this example, all the units cancel out thus K_c has no units.

For the Haber process which is the manufacture of ammonia



$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

The units for would be

$$K_c = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})^3}$$
$$= \frac{1}{(\text{mol dm}^{-3})^2} \text{ or } \text{mol}^{-2} \text{ dm}^6$$

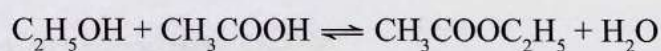
Calculating a value of K_c

When calculating a value for the equilibrium constant the concentration of at least one of the reactants or products must be known. This is very important in calculating the concentration of all the other species at equilibrium. Consider the following example:

Ethanol and ethanoic acid were mixed and allowed to reach equilibrium at temperature T. The mixture which initially contained one mole ethanol and two moles of ethanoic acid in a dm^3 now contains 0.35 mol dm^{-3} of ester at equilibrium.

- Calculate the concentration of the other species in the equilibrium mixture.
- Determine K_c and state its units.

The equation for the reaction is



Mole ratio	1 mole	1 mole	1 mole	1 mole
Initial conc./ mol dm^{-3}	1	2	0	0
Conc. at equilibrium/ mol dm^{-3}	x	y	0.35	z

Since 0.35 mole of ester was formed, the same amount of water will be produced i.e. 0.35 mole of water.

Initially there was 1 mole $\text{C}_2\text{H}_5\text{OH}$, since 0.35 mole of this was converted to the ester, the number of moles remaining at equilibrium is $1 - 0.35 = 0.65 \text{ mol dm}^{-3}$

Initially there were 2 moles CH_3COOH , since 0.35 mole of the acid was used to produce the ester, the amount remaining at equilibrium is $2 - 0.35 = 1.65 \text{ moles}$.

Now that the concentration of all the species at equilibrium is known, the next step is to write the expression for K_c .

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]}{[\text{C}_2\text{H}_5\text{OH}] [\text{CH}_3\text{COOH}]}$$



Substitute the following values in the equation

Ester = 0.35 mol dm^{-3}
Water = 0.35 mol dm^{-3}
Alcohol = 0.65 mol dm^{-3}
Acid = 1.65 mol dm^{-3}

$$\begin{aligned}K_c &= \frac{0.35 \text{ mol dm}^{-3} \times 0.35 \text{ mol dm}^{-3}}{0.65 \text{ mol dm}^{-3} \times 1.65 \text{ mol dm}^{-3}} \\&= \frac{0.1225}{1.0725} \\&= 0.1142\end{aligned}$$

There are no units since they cancel.

Experimental determination of the equilibrium constant

To determine the equilibrium constant of a reaction a number of steps must be followed. The following example involving ethanoic acid and ethanol to produce ethyl ethanoate and water is used to illustrate the steps involved.

The balanced equation for the reaction is



First the experiment is set up using known concentrations of ethanol and ethanoic acid. The mixture is covered and allowed to reach equilibrium.

After equilibrium has been achieved, the concentration of one of the reactants is determined. Various techniques are available such as colorimetry (for coloured reactants or products), pressure measurements (for reactants involving gases) or volumetric analysis (for reactions involving acids and bases). In the esterification reaction, the concentration of the ethanoic acid at equilibrium can be found by volumetric analysis using standardized aqueous sodium hydroxide with phenolphthalein indicator.

Once the concentration of one of the reactants at equilibrium is determined, the equilibrium concentration of the other species in the reaction can then be calculated. The concentration of all species must be calculated in mol dm^{-3} .

The values are then substituted in the equation for K_c . The equilibrium constant is calculated and the units are worked out.

The equilibrium constant for gaseous systems K_p

It is more convenient to measure the pressure of gases at equilibrium rather than concentrations. Thus K_p is used as the equilibrium constant for gaseous systems. The subscript p refers to the pressure of gases. The total pressure of a mixture of gases is the sum of individual pressure of each gas in the system. The individual pressure is referred to as the partial pressures of the gas in the mixture. The symbol used to express partial pressure is p.

Thus for a mixture of gases A, B and C, the total pressure is the sum of the partial pressures.

$$P_{\text{total}} = p_A + p_B + p_C$$

The partial pressure (p) of a gas

$$= \frac{\text{number of moles of gas}}{\text{total number of moles}} \times \text{total pressure}$$

Therefore

$$p = X P_{\text{total}} \quad \text{where } X \text{ is the mole fraction}$$

Thus the partial pressure of gas A is

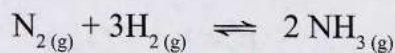
$$p_A = X_A P_{\text{total}}$$

where p_A is the partial pressure of a gas A

X_A is the mole fraction of the gas A

P_{total} is the total pressure

Consider the the reaction of nitrogen and hydrogen in the Haber process



$$K_p = \frac{(p\text{NH}_3)_{\text{eq}}^2}{(p\text{N}_2)_{\text{eq}} (p\text{H}_2)_{\text{eq}}^3}$$

Example

2.5 atm of nitrogen gas and 3 atm of hydrogen gas were placed in an empty container and allowed to reach equilibrium. It was found that the pressure of the nitrogen gas decreased by 0.5 atm. Estimate the value of K_p for this system.

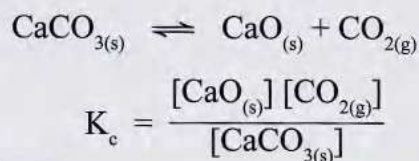
	$3\text{H}_{2(g)}$	$+$	$\text{N}_{2(g)}$	$\rightleftharpoons$	$2\text{NH}_{3(g)}$
Mole ratio	3moles		1mole		2moles
Initial Pressure (atm)	3.0		2.5		0
Change in Pressure (atm)	1.5		0.5		1
Equilibrium Pressure (atm)	1.5		2.0		1

$$\begin{aligned}
 K_p &= \frac{(\text{pNH}_3)_{\text{eq}}^2}{(\text{pN}_2)_{\text{eq}} (\text{pH}_2)_{\text{eq}}^3} \\
 &= \frac{(1\text{atm})^2}{(2\text{atm}) \times (1.5\text{atm})^3} \\
 &= 0.15\text{atm}^{-2}
 \end{aligned}$$

Heterogenous reactions

The equilibria met so far are called **homogeneous equilibria** i.e. all the chemical species are in the same phase. The species were either all dissolved or were all gases. However, equilibria in which the species are not in the same phase are referred to as **heterogeneous equilibria**. Examples of heterogeneous equilibria are ionic compounds partially dissolved in water and the decomposition of calcium carbonate.

When writing an expression for the equilibrium constant for a heterogeneous equilibrium the concentrations of solids are not included in the equilibrium expression. The concentration of a substance is the number of moles per unit volume. For solids, the concentration would thus be equivalent to its density, i.e. mass per unit volume. Since the density of the solid does not change, then the concentration of the solid remains constant. For example, in the decomposition of calcium carbonate



Since the concentrations of the solids are constant, the equilibrium constant can be written as

$$K'_c = [\text{CO}_2]$$

where K'_c is a new constant which takes the concentrations of the solids into consideration.

Similarly K_p for the reaction can be written as

$$K_p = [\text{CO}_2]$$



FACTORS AFFECTING EQUILIBRIUM

When equilibrium mixtures are subjected to small changes in conditions such as concentration, temperature and pressure, the equilibrium tends to shift so as to minimize the effect of the change. This was investigated by Henri Le Chatelier in 1888 and is referred to as Le Chatelier's principle.

Effect of concentration

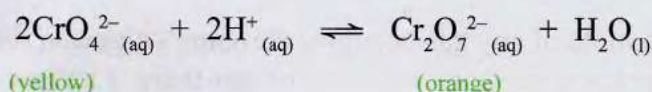
Consider the reaction at a fixed temperature



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

If either A or B is added to the mixture at equilibrium, more C and D would form so that the new concentration ratio in the equilibrium expression would be the same for K_c . The equilibrium is referred to as 'shifting to the right'. If either C or D is added to the equilibrium mixture, more A and B would form shifting the equilibrium to the left so that the new concentration ratio in the equilibrium expression would be the same for K_c .

The effect of concentration on equilibrium can be seen in the acidification of sodium chromate(VI).



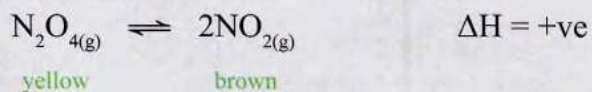
The yellow solution of sodium chromate(VI) turns orange when acid is added. As the concentration of H^+ ions increases, equilibrium shifts to the right and chromate(IV) ions are converted to dichromate(VI) ions. On adding an alkali, the H^+ ions are removed and the equilibrium shifts to the left turning the solution yellow again.

Effect of temperature

A change in temperature causes a shift in equilibrium as well as a change in the value of the equilibrium constant. The effect temperature has depends on whether the reaction is endothermic or exothermic. Reactions which are endothermic in the forward direction are exothermic in the backward direction. For example, the reaction involving the conversion of dinitrogen tetroxide to nitrogen dioxide is endothermic in the forward direction and



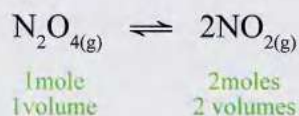
exothermic in the backward direction.



An increase in temperature shifts the equilibrium towards the endothermic direction (to the right in this case) and increases the value of K_c or K_p . Therefore the colour changes from yellow to brown. A decrease in temperature shifts the equilibrium towards the exothermic direction (to the left in this case) and decreases the value of K_c or K_p . Here the colour changes from brown to yellow.

Effect of pressure

In reactions where there are changes in volumes, a change in pressure causes a shift in equilibrium but the value of the equilibrium constant remains the same. In the reaction involving the conversion of dinitrogen tetroxide to nitrogen dioxide, there is an increase in the number of moles in the forward direction.



$$K_p = \frac{(p\text{NO}_2)_{\text{eq}}^2}{(p\text{N}_2\text{O}_4)_{\text{eq}}}$$

Since one mole of any gas occupies the same volume at the same temperature and pressure, we can say that there is an increase in volume in the forward direction. So with an increase in pressure, there would be a decrease in volume as molecules are pushed closer together. Thus equilibrium would shift in the direction of the smaller volume i.e. towards the left. Therefore an increase in pressure would result in more dinitrogen tetroxide being formed so that the new pressure ratio in the equilibrium expression would be the same for K_p .

A decrease in pressure would result in an increase in volume. Thus equilibrium would shift in the direction of the larger volume i.e. towards the right. Therefore a decrease in pressure would result in more nitrogen dioxide being formed.

Catalyst

A catalyst alters the rate of a chemical reaction. In a reversible reaction, it can increase the rate of the forward and backward



reaction to the same extent so that equilibrium is reached more rapidly. However, it has no effect on the position of equilibrium and does not change the value of the equilibrium constant.

Application of Le Chatelier's principle to industrial processes such as the Haber process and the Contact process are discussed later on under the section of 'Industry and the Environment'.

Facts about the equilibrium constant K_c

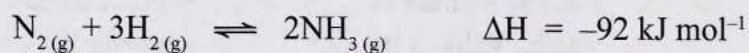
- The equilibrium law only applies to systems that are in dynamic equilibrium.
- K_c is very sensitive to changes in temperature. It is only constant when temperature is constant. If temperature changes, the K_c value changes.
- Changes in concentration and pressure do not affect K_c since the equilibrium is adjusted to ensure that K_c remains constant. For example, if the concentration of reactants increases the concentration of products would tend to increase. Eventually the system adjusts itself to restore equilibrium such that the concentrations of the reactants and products give the same K_c value.
- K_c gives an indication as to the extent of a chemical reaction. A large K_c value indicates that there is a larger proportion of products to reactants. A small value indicates that there are more reactants than products. K_c gives no indication as to how fast the reaction will occur.
- K_c values can be compared with each other. It indicates whether one reaction will go to completion more than another. When sulphur dioxide reacts with oxygen, the reaction takes a long time but the K_c is large. At the same temperature, when nitrogen monoxide reacts with oxygen to form nitrogen dioxide, the reaction is rapid but the K_c value is smaller. The K_c values indicate that the reaction of sulphur dioxide with oxygen goes to completion more than that of nitrogen oxide with oxygen.





Questions

1. What do you understand by the following terms:
 - (a) dynamic equilibrium
 - (b) equilibrium constant
 - (c) equilibrium law
 - (d) heterogeneous equilibria
2.
 - (a) State four characteristic properties of a system in dynamic equilibrium.
 - (b) Write an equation for the equilibrium reaction for the decomposition of phosphorous (V) chloride to phosphorous (III) chloride and chlorine.
 - (c) Write an expression for the equilibrium constant for the reaction in (b) above. State the units of the equilibrium constant.
3. The equation below represents the reaction for the production of ammonia.



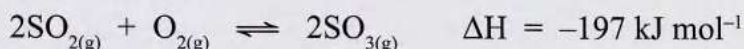
Equilibrium is established with the gases having the following partial pressures in atmospheres.

gas	p/atm
N_2	2
H_2	3
NH_3	3

- (a) Write an expression for the equilibrium constant for the reaction.
- (b) Calculate a value for the equilibrium constant and state its units.
- (c) Explain the effect of an increase temperature on the value of the equilibrium constant.

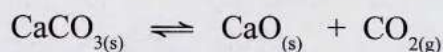


4. (a) State Le Chatelier's principle.
(b) State two factors that can disturb a system in equilibrium.
(c) Sulphur dioxide is converted to sulphur trioxide in the Contact process according to the equation below.



State the effect of the following on the position of equilibrium in the Contact process:

- (i) an increase in temperature
 - (ii) increase in pressure
 - (iii) use of a catalyst
5. Calcium carbonate decomposes according to the equation below.



Applying Le Chatelier's principle, explain the effect on the position of equilibrium when the following occurs:

- (i) the concentration of CaCO_3 is increased
 - (ii) CO_2 is removed from the system
6. 2 moles of N_2O_4 was placed in an empty 1 dm^3 bottle and allowed to reach equilibrium according to the equation:



At equilibrium, 1.2 moles of N_2O_4 dissociated. Calculate the value of the equilibrium constant for the reaction at that temperature.

7. A mixture of 0.5 mole of ethanoic acid and 1 mole of ethanol in 1 dm^3 was allowed to reach equilibrium at room temperature. The equilibrium mixture was quickly titrated and 40 cm^3 of 2 mol dm^{-3} sodium hydroxide was used in the titration.

- (a) Why was the reaction titrated quickly?
- (b) Using the titration results, calculate the number of moles of
 - (i) ethanoic acid left in the equilibrium mixture.
 - (ii) ethanoic acid reacted.
 - (iii) ethanol reacted.
 - (iv) ethanol left in the equilibrium mixture.
- (c) Calculate the equilibrium constant for the reaction between ethanoic acid and ethanol at room temperature.

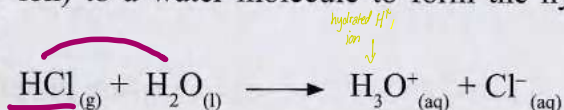


THE BRONSTED-LOWRY THEORY OF ACIDS AND BASES

The Bronsted-Lowry theory of acids and bases states that

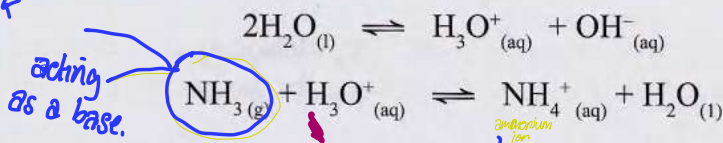
- an acid is a proton (H^+ ion) donor.
- a base is a proton (H^+ ion) acceptor.

When hydrogen chloride gas dissolves in water to produce hydrochloric acid, the hydrogen chloride molecule donates a proton (H^+ ion) to a water molecule to form the hydroxonium ion, H_3O^+ .



When hydrogen chloride gas dissolves in water, almost all of it ionizes in water to produce hydroxonium ions and chloride ions. Therefore hydrochloric acid is described as a strong acid.

When ammonia dissolves in water to produce ammonium hydroxide, the ammonia accepts a proton (H^+ ion) from the hydroxonium ion, H_3O^+ .

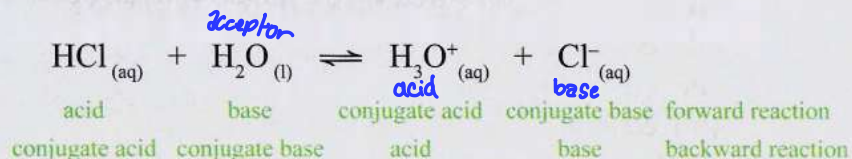


Ammonia accepts a proton to form the ammonium ion and its therefore acting as a base. When ammonia gas dissolves in water, only some of it ionizes in water therefore ammonia is described as a weak base.



CONJUGATE ACID-BASE PAIR

The reaction between HCl and water is reversible only to a minor extent. Consider the reversible reaction



In the forward reaction, the HCl is an acid because it donates



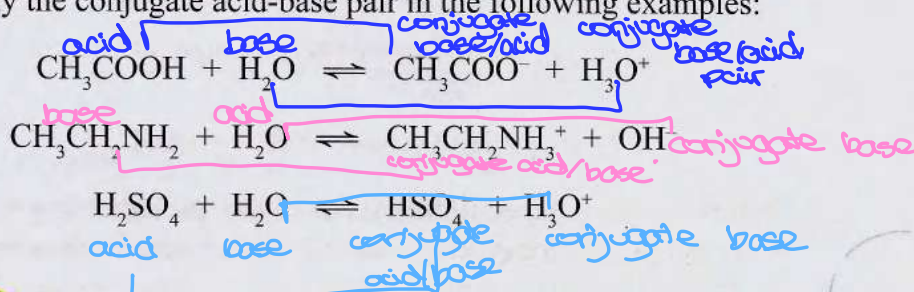
a proton (H^+ ion) to the water. The water is a base because it accepts a proton from the HCl .

In the backward reaction, the H_3O^+ is an acid because it donates a proton (H^+ ion) to the Cl^- ion. The Cl^- ion is a base because it accepts a proton from the H_3O^+ .

When the acid, HCl , donates a proton it forms the base, Cl^- . When the base, Cl^- , accepts a proton, it reforms the acid, HCl . Thus HCl and Cl^- are referred to as a **conjugate acid-base pair**.

Cl^- is the conjugate base of the acid HCl , while HCl is the conjugate acid of the base Cl^- . Similarly with the water as the base, the hydroxonium ion is its conjugate acid and with the hydroxonium ion as the acid, the water is its conjugate base.

Identify the conjugate acid-base pair in the following examples:



THE STRENGTH OF ACID AND BASE

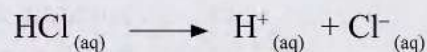
Acids

Acids are classified into two categories based on their ability to ionize in aqueous solutions. These are strong acids and weak acids.

A strong acid is defined as an acid that **ionizes completely** in aqueous solutions producing a high concentration of hydrogen ions.



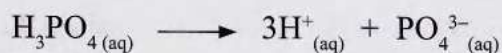
Notice that the arrow points in one direction only. Strong acids are described in terms of their basicity or proticity. The **basicity or proticity** of an acid refers to the number of moles of H^+ ions that are produced per mole of acid.



1 mole of hydrochloric acid produces 1 mole of H^+ and it is said to be monobasic or monoprotic.



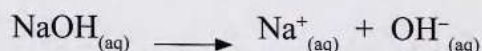
1 mole of sulphuric acid produces 2 moles of H^+ per mole of acid and it is said to be dibasic or diprotic.



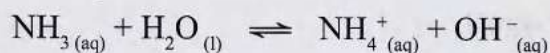
1 mole of phosphoric acid produces 3 moles of H^+ per mole of acid and it is said to be tribasic or triprotic. Phosphoric acid is present in the soft drink Coca Cola, which explains the acidity of this beverage.

Bases

Bases are also classified as strong and weak bases. Bases that dissolve in water are referred to as alkali. Strong bases ionize completely in water. For example



Weak bases do not ionize completely in aqueous solutions. For example



In this reaction, the equilibrium lies to the left indicating that the ammonia is not completely ionized. Only a small concentration of hydroxide ions is generated in solution and the solution is slightly alkaline.



CALCULATING pH

The pH scale

The relative strengths of acids can be compared by measuring the concentration of hydrogen ions. The concentration of hydrogen ions in solution can range from about 10^{-15} to 10 mol dm^{-3} . Using a logarithmic scale can reduce this wide range to a narrow range. Using negative logarithmic would produce a positive value for these concentrations. The pH scale is thus used to measure acidity and range from 0 to 14. It is the negative logarithm to base ten of the concentration of hydrogen ion in a solution.

$$\text{pH} = -\log_{10} [\text{H}^+]$$

The lower the pH, the more acidic is a solution. A change in pH from 2 to 3 represents a 10 time decrease in the concentration H^+ ions, and a change from 2 to 4 represents a one-hundred (10×10) time decrease in the concentration H^+ ions.



[H ⁺]	10 ⁻¹⁴	10 ⁻¹²	10 ⁻¹⁰	10 ⁻⁸	10 ⁻⁷	10 ⁻⁶	10 ⁻⁴	10 ⁻²	10 ⁻⁰
pH	14	12	10	8	7	6	4	2	0
	Strongly Alkaline		Alkaline		Neutral		Acidic		Strongly Acidic

Fig. 9.1 The pH scale

The concentration of the hydroxide ion can be measured similarly using a pOH scale.

$$\text{pOH} = -\log_{10} [\text{OH}^-_{(\text{aq})}]$$

Relationship between pH and pOH

The concentration of hydrogen ions in water at 25°C is 10⁻⁷ mol dm⁻³. The pH of water is

$$\begin{aligned}\text{pH} &= -\log_{10} [\text{H}^+] \\ &= -\log_{10} [10^{-7}] \\ &= 7\end{aligned}$$

The concentration of hydroxide ions in water at 25°C is 10⁻⁷ mol dm⁻³. The pOH of water is

$$\begin{aligned}\text{pOH} &= -\log_{10} [\text{OH}^-] \\ &= -\log_{10} [10^{-7}] \\ &= 7\end{aligned}$$

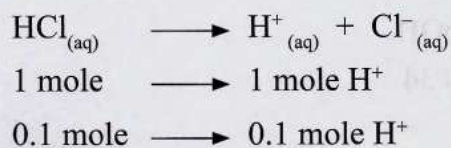
Thus pH + pOH = 14

Calculating the pH of a strong acid

Strong acids are fully dissociated in aqueous solution and the concentration of H⁺ ions can be found using stoichiometry.

Example 1

Calculate the pH of a 0.1 mol dm⁻³ HCl solution.

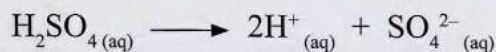


$$\begin{aligned}\text{Therefore pH} &= -\log_{10} [\text{H}^+] \\ &= -\log_{10} (0.1) \\ &= 1\end{aligned}$$



Example 2

Calculate the pH of a $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution.



$$\begin{aligned}\text{Therefore pH} &= -\log_{10} [\text{H}^+] \\ &= -\log_{10} (0.2) \\ &= 0.7\end{aligned}$$

Calculating the pH of a strong base

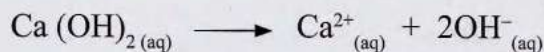
To calculate the pH of a strong base it is necessary to determine the hydroxide ion concentration in mole per dm^{-3} and then determine the pOH using $\text{pOH} = -\log_{10} [\text{OH}^-]$. From here pH can then be determined using

$$\text{pH} = 14 - \text{pOH}$$

Example 3

Calculate the pH of a $0.23 \text{ mol dm}^{-3} \text{ Ca(OH)}_2$ solution.

First determine OH^- ion concentration



Next calculate pOH

$$\begin{aligned}\text{pOH} &= -\log_{10} [\text{OH}^-] \\ &= -\log_{10} (0.46) \\ &= 0.34\end{aligned}$$

Then determine the pH using

$$\begin{aligned}\text{pH} &= 14 - \text{pOH} \\ &= 14 - 0.34 \\ &= 13.66\end{aligned}$$

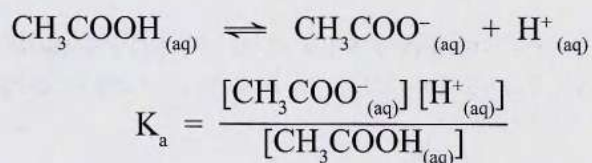


THE ACID DISSOCIATION CONSTANT (K_a)

A weak acid dissociates only to a small extent in aqueous solution until equilibrium is achieved. The equilibrium expression written



for the reaction is called the acid dissociation constant (K_a). The acid dissociation constant (K_a) can be used to compare the strengths of acids. Consider the reaction in which the weak acid, ethanoic acid dissolves in water



Since water is the solvent, it is in large excess and is excluded from the equation. Water is only included in an equilibrium expression if it is a reactant or a product in a chemical reaction. Thus K_a can be written as

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

If the concentration of the acid is known together with the concentration of the ions, a value of K_a can be easily calculated. In the above example K_a has units of mol dm^{-3} . **A large K_a value means that the acid is highly dissociated therefore it is a strong acid.**

The $\text{p}K_a$ can be calculated from the negative logarithm to base ten of K_a

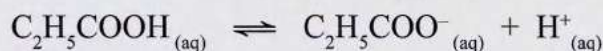
$$\text{p}K_a = -\log_{10} K_a$$

The larger the K_a value, the smaller is the $\text{p}K_a$ value and the stronger the acid.

Calculating the pH of a weak acid

Calculate the pH of a solution of propanoic acid of concentration 0.2 mol dm^{-3} , given that the $\text{p}K_a$ of propanoic acid is 4.82

The equation for the reaction is



Initial conc. 0.2 mole

0

0

At eqm. 0.2 - x

x

x

At equilibrium only a small number of molecules of the acid dissociate to produce the $\text{C}_2\text{H}_5\text{COO}^-$ ions and H^+ ions. If we assume that x moles of the acid has dissociated to produce x moles of the $\text{C}_2\text{H}_5\text{COO}^-$ ions and x moles of H^+ ions, then



$$K_a = \frac{[C_2H_5COO^-][H^+]}{[C_2H_5COOH]}$$

$$= \frac{(x)(x)}{(0.2 - x)}$$

Since propanoic acid is a weak acid and little dissociation of the acid occurs, the value of $0.2 - x$ is approximately equal to 0.2.

So

$$K_a = \frac{x^2}{0.2}$$

$$K_a = \text{antilog}_{10}(-pK_a)$$

$$= \text{antilog}_{10}(-4.82)$$

$$= 1.513 \times 10^{-5}$$

Thus

$$1.513 \times 10^{-5} = \frac{x^2}{0.2}$$

The H^+ ions concentration, $x = 1.740 \times 10^{-3} \text{ mol dm}^{-3}$.

Hence

$$pH = -\log_{10} [H^+]$$

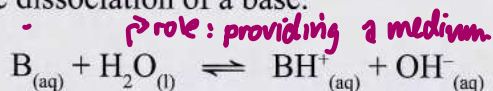
$$= -\log_{10} (1.74 \times 10^{-3})$$

$$= 2.76$$



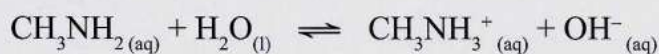
THE BASE DISSOCIATION CONSTANT (K_b)

Base dissociation constants can be used to compare the strengths of bases. Just as acids, an equilibrium expression can also be written for the dissociation of a base.



$$K_b = \frac{[BH^+_{(aq)}][OH^-_{(aq)}]}{[B_{(aq)}]}$$

Weak bases such as methylamine are proton acceptors. Consider the reaction of methylamine with water



$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

Taking negative logarithms to base 10 gives

$$pK_b = -\log_{10} (K_b)$$

A small K_b value means that the base is dissociated to a small

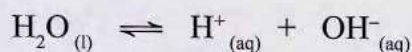


extent therefore it is a weak base. The stronger the base the larger is the K_b and hence the smaller the pK_b value.



THE IONIC PRODUCT OF WATER

Water at 25°C dissociates to a very small extent producing a minute quantity of the hydrogen cation and the hydroxide anion. An equilibrium expression can be written for the dissociation as dynamic equilibrium is achieved.



$$K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$K_c [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

K_c is a constant and the concentration of water is considered to be a constant because so little of the water has dissociated that the change is negligible. Two constants when multiplied together give us a new constant, which we call K_w , the **ionic product of water**. At 25°C it has been found that the concentration of H^+ and OH^- is $1 \times 10^{-7} \text{ mol dm}^{-3}$ respectively

$$\begin{aligned} K_w &= [\text{H}^+][\text{OH}^-] \\ &= (10^{-7} \text{ mol dm}^{-3}) \times (10^{-7} \text{ mol dm}^{-3}) \\ &= 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \end{aligned}$$

The relationship between K_a and K_b

The relationship between K_a of the conjugate acid and K_b of the base is as follows:

Let BH^+ be the conjugate acid of a base, then the equilibrium constant (K_a) for the conjugate acid is

$$\begin{aligned} \text{BH}^+ &\rightleftharpoons \text{B} + \text{H}^+ \\ K_a &= \frac{[\text{B}][\text{H}^+]}{[\text{BH}^+]} \\ &= \frac{[\text{B}][\text{H}^+][\text{OH}^-]}{[\text{BH}^+][\text{OH}^-]} \\ &= \frac{[\text{B}]}{[\text{BH}^+][\text{OH}^-]} [\text{H}^+][\text{OH}^-] \\ &= \frac{1}{K_b} K_w \end{aligned}$$

Thus



$$K_a K_b = K_w$$

Taking negative $\log_{10}$

$$pK_a + pK_b = pK_w$$

$$pK_w = 14 \text{ at } 25^\circ\text{C}$$

Therefore

$$pK_a + pK_b = 14$$

The above equations can be used to calculate the pH of a weak base. Consider the following example:

What is the pH of methylamine of concentration 0.45 mol dm⁻³ given the pK_a of CH_3NH_3^+ to be 9.25?

Step 1: If we have pK_a then we calculate pK_b

$$pK_a + pK_b = 14$$

$$9.25 + pK_b = 14$$

$$pK_b = 4.75$$

Step 2: Calculate K_b

$$K_b = \text{antilog}(-pK_b)$$

$$= \text{antilog}(-4.75)$$

$$= 1.775 \times 10^{-5} \text{ mol dm}^{-3}$$

Step 3: Write an equation for reaction and insert the data given in the question



Initial conc.	0.45	excess	0	0
At equilibrium	0.45 - x	excess	x	x

$$K_b = \frac{x^2}{0.45 - x}$$

Since methylamine is a weak base and little dissociation occurs, the value of $0.45 - x$ is approximately equal to 0.45.

Therefore

$$\frac{x^2}{0.45} = 1.775 \times 10^{-5}$$

$$x = 2.829 \times 10^{-3} \text{ mol dm}^{-3}$$

$$= [\text{OH}^-]$$

$$pK_a + pK_b = 14$$

$$pK_b$$

$$K_b = \text{antilog}(-pK_b)$$

So

$$\begin{aligned} \text{pOH} &= -\log_{10} [\text{OH}^-] \\ &= -\log_{10} [2.829 \times 10^{-3}] \\ &= 2.55 \end{aligned}$$

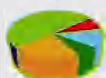
$$\begin{aligned} \text{pH} + \text{pOH} &= 14 \\ \text{pH} &= 14 - \text{pOH} \\ &= 14 - 2.55 \\ &= 11.45 \end{aligned}$$

pH of a weak base =

$$\text{pOH} = -\log_{10} \sqrt{K_b \times [\text{weak base}]}$$

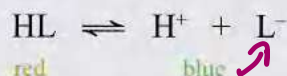
to find pH use

$$\text{pOH} + \text{pH} = 14$$



ACID-BASE INDICATORS

An acid-base indicator is a conjugate acid-base pair in which the acid is a different colour to the base. Using litmus as an example we can write the undissociated molecule as HL and the dissociated molecules as H^+ and L^- at equilibrium.



When an acid is added, there is an increase in the concentration of H^+ ions, equilibrium shifts to the left and the colour changes to red. When an alkali is added, there is a decrease in the concentration of H^+ ions as H^+ ions react with the OH^- ions of the alkali to form water. The equilibrium shifts to the right and the colour changes from red to blue.

Indicators do not change colour at a specific hydrogen ion concentration but rather over a narrow range of hydrogen ion concentrations. This range is called the **pH range of the indicator**.

Fig. 9.1

Indicator	Colour change	pH at end point
Methyl orange	Orange $\rightarrow$ yellow	3.7
Litmus	Red $\rightarrow$ blue	6.5
Bromothymol blue	Yellow $\rightarrow$ blue	7
Phenolphthalein	Colourless $\rightarrow$ pink	9.1

Table 9.2

Colour change and end-point of some indicators

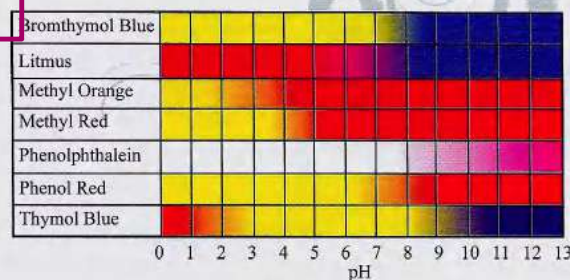
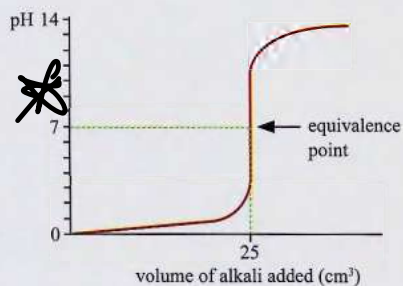


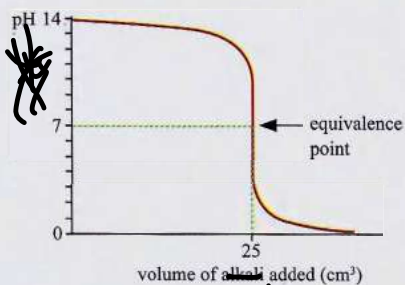
Fig. 9.1

Indicator range of some indicators

Indicators can be used to test the acidity and alkalinity of solutions and to determine the end point of a titration. The end point is a signal that marks the completion of the reaction in the titration. When an indicator is used in a titration, it is the point at which



(a) alkali added to acid



(b) acid added to alkali

Fig. 9.2

Titration curves of a strong base versus a strong acid

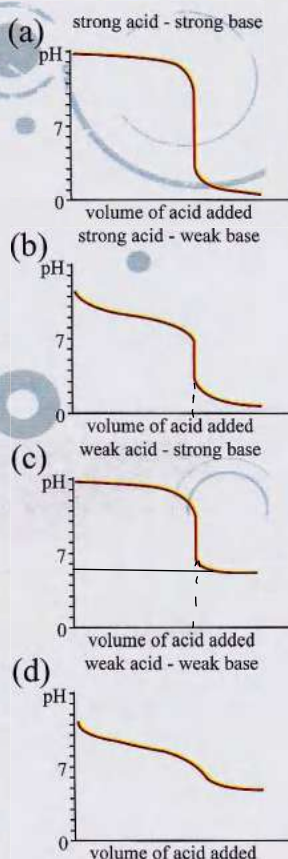


Fig. 9.3

Strength of the acid and alkali gives different titrations curves

the colour of the indicator changes in the titration. The end point must coincide with the equivalence point in the titration. **The equivalence point** is the point where the number of moles of acid equals the number of moles of base in the titration.



pH CHANGES DURING TITRATIONS

The pH of a solution changes during a titration as an acid is added to an alkali or vice versa. A plot of the changes in pH as an acid is added to an alkali or vice versa is known as a **titration curve**. In the titration curves in fig. 9.2, (a) shows how the pH of the solution changes when an alkali is added to an acid during titration, while (b) shows how the pH of the solution changes when an acid is added to an alkali during titration. The pH changes sharply by several units at the equivalence point.

Fig. 9.2

In the curve (a), the pH changes gradually as the alkali is added to the acid. As end point is approached, the pH of the solution increases sharply. Once the endpoint has been passed, the pH change slows down again. The midpoint of the most vertical part of the graph will correspond to equivalence point.

Not all titration curves are the same. The graphs in fig. 9.2 show the titration curves using a strong base and a strong acid. Graphs differ in shape depending upon whether the acid or alkali that is being titrated is strong or weak. See fig. 9.3(a) –(d).

Fig. 9.3

Any acid-base indicator that changes colour at a pH in the vertical part of the graph is suitable to detect the titration. Any indicator which changes colour between pH 3 to 11 is suitable for a strong acid-strong base titration. Both methyl orange and phenolphthalein could be used.

An indicator which changes colour between pH 3 to 7 is suitable for a strong acid-weak base titration. Methyl orange which changes colour at pH 3.7 is suitable for a strong acid-weak base titration, however, phenolphthalein which changes colour at pH 9.1 is not a suitable indicator.

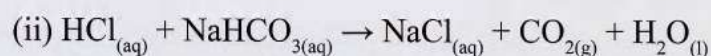
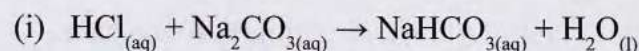
For a weak acid-strong base titration, an indicator which changes colour between pH 7 to 11 is suitable. Methyl orange which changes colour at pH 3.7 is not suitable whereas phenolphthalein which changes colour at pH 9.1 is a suitable indicator.

In the titration curve of a weak acid-weak base titration, the change of pH is too gradual to show a distinct end point using acid-base indicators. Instead conductometric titration can be used to find the end-point.

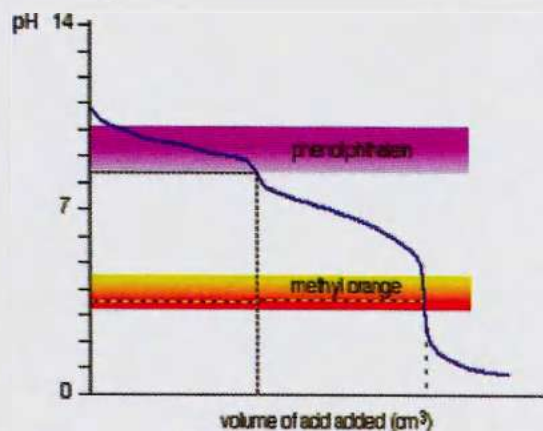


TITRATION CURVE WITH TWO EQUIVALENCE POINTS

Consider the titration of $\text{HCl}_{(\text{aq})}$ with $\text{Na}_2\text{CO}_{3(\text{aq})}$.
The reaction takes place in two stages:



The equivalence point of reaction (i) is alkaline whereas that of reaction (ii) is acidic. Thus the titration curve shows two equivalence points corresponding to the above two stages. Phenolphthalein is a suitable indicator for the first stage of the reaction while methyl orange is suitable for the second stage. It must be noted that the titre value with methyl orange will be twice that of the value with phenolphthalein.





Questions

- Explain the difference between a *weak base* and a *strong base* using the Bronsted-Lowry theory.
 - Ammonia forms a weak basic solution in water.
 - Write an equation for the reaction between ammonia and water.
 - Write an expression for the equilibrium constant for the reaction.
- Use the equilibrium systems below to answer (a) to (e) below.



- Explain the meaning of the term conjugate acid-base pair.
 - Write the formula of the conjugate acid of $\text{HCO}_3^{-}{}_{(\text{aq})}$.
 - Write the formula of the conjugate base of $\text{HCO}_3^{-}{}_{(\text{aq})}$.
 - Which species is considered the strongest acid?
 - Which species is considered the strongest base?
- Define the following:
 - K_a
 - $\text{p}K_a$
 - The equation and acid dissociation constant for $\text{H}_2\text{CO}_{3(\text{aq})}$ is given below.



$$K_a = 4.5 \times 10^{-7} \text{ mol dm}^{-3}$$

Calculate the $\text{p}K_a$ value of $\text{H}_2\text{CO}_{3(\text{aq})}$.

- Define the term pH
 - Calculate the pH of a solution of hydrochloric acid of concentration 0.5 mol dm^{-3} .
 - Calculate the pH of a solution of aqueous ammonia of concentration 0.1 mol dm^{-3} given that the K_b of aqueous ammonia is 1.8×10^{-5} at experimental temperatures.



- (d) Account for the different pK_b values of the bases given below.

Base	pK_b
NH_3	4.75
CH_3NH_2	3.43
$C_2H_5NH_2$	3.37

5. Define the following terms:

- (a) end-point
- (b) equivalence point
- (c) indicator range

State the relationship between the three terms above.

6. (a) Sketch the titration curve for the reaction between sodium hydroxide and ethanoic acid. Suggest an indicator that will not be effective in this titration giving reasons for your answer.
- (b) Explain why acid-base indicators are not suitable to determine the end-point of weak acid-weak base titration. Suggest a suitable method that can be used to find the end-point of such a reaction.
7. (a) Derive the relationship for the ionic product of water (K_w).
- (b) State the units for the ionic product of water (K_w).
- (c) How does the value of K_w vary with temperature?
- (d) Explain why water at $25^\circ C$ has a pH of 7.



A buffer is defined as a solution which resists changes in pH with the addition of a small amount of acid or alkali. In simple terms, if a solution has the ability to maintain its pH value when a small amount of acid or alkali is added, then it is referred to as a buffer solution. There are naturally occurring buffers in the body which ensure that the pH of the body remains constant. These include the carbonate/hydrogencarbonate buffer system ($\text{CO}_3^{2-}/\text{HCO}_3^-$) as well as the amino acids in the body which exists as zwitterions and have the capacity to accept or give up H^+ ions to maintain pH.

Synthetic buffers are produced in the laboratory and are of two types:

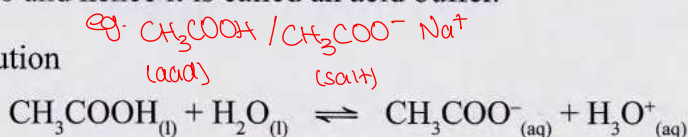
- Acid buffers
- Basic buffers.



ACID BUFFERS

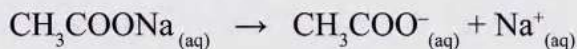
An acid buffer consists of a weak acid (e.g. ethanoic acid) and a salt that gives the conjugate base of the weak acid (e.g. sodium ethanoate). The pH of this buffer is less than 7, usually between 4 and 6 and hence it is called an acid buffer.

In solution



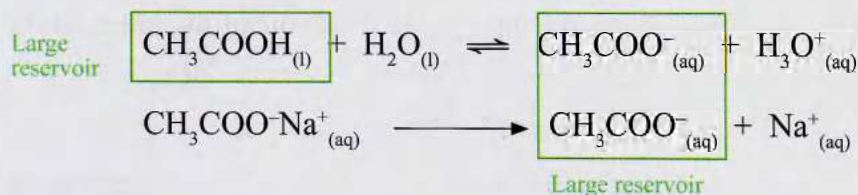
Since the ethanoic acid is only slightly dissociated there is a large amount of the undissociated ethanoic acid molecules which is referred to as a large reservoir of ethanoic acid.

The sodium ethanoate ionizes completely according to the equation



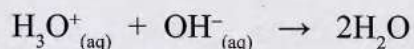
Salts such as sodium ethanoate are completely dissociated in aqueous solutions producing a large reservoir of the ethanoate ions. This overall ionization can be expressed as





On addition of a small amount of base to the buffer

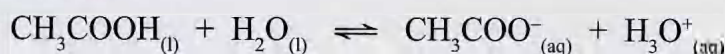
The excess $\text{OH}^-_{(aq)}$ ions combine with the $\text{H}_3\text{O}^+_{(aq)}$ ions to produce water.



This reduces the concentration of H_3O^+ ions in the buffer. The equilibrium shifts to the right causing ethanoic acid molecules to dissociate to restore the concentration of H_3O^+ ions to its original value. Thus the pH of the solution remains relatively constant. This is an application of Le Chatelier's principle. Note that the pH may change but to a very small extent, that is, the change is considered to be negligible.

On addition of a small amount of acid to the buffer

On addition of the acid, the concentration H_3O^+ ions will increase. This shifts the equilibrium to the left. The additional H_3O^+ ions combine with the large reservoir of ethanoate ions to produce ethanoic acid.

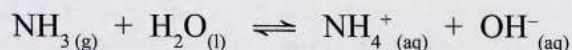


Since the excess H_3O^+ ions are removed, the pH is maintained. The small increase in the concentration of the ethanoic acid is considered to be negligible since a large reservoir of acid exists in the buffer solution.



BASIC BUFFERS

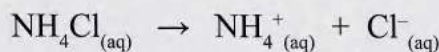
A basic buffer consists of a weak base and a salt that gives the conjugate acid of the weak base (e.g. NH_3 and NH_4Cl). A basic buffer usually has a pH value between 8 and 10. In the ammonia, ammonium chloride system, the weak base ammonia ionizes incompletely in aqueous solutions leaving a large reservoir of the unprotonated ammonia molecule.



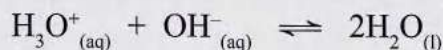
Ammonium chloride is a salt and dissociates completely in



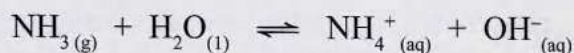
aqueous solutions producing a large reservoir of the ammonium ion.



If a small amount of acid is added to this buffer, the concentration of H_3O^+ ions increases. The excess H_3O^+ ions react with the OH^- ions from the equilibrium mixture to produce water.



This reaction results in the removal of the H_3O^+ ions thus the pH is maintained. The equilibrium in the reaction below shifts to the right to restore the OH^- ions concentration.



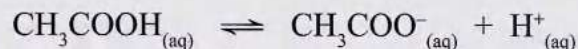
Thus the concentration of the undissociated NH_3 decreases slightly.

If a small amount of base is added to the buffer, the increase in concentration of the OH^- ions causes the equilibrium in the reaction below to shift to the left. The excess OH^- ions are removed as more undissociated ammonia is formed thus maintaining the pH of the solution.



CALCULATING THE pH OF A BUFFER SOLUTION

Ethanoic acid dissociates according to the following equation:



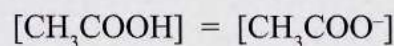
An expression for the acid dissociation constant can be written as

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{Equation 1}$$

Making $[\text{H}^+]$ the subject of the formula

$$[\text{H}^+] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \quad \text{Equation 2}$$

If a buffer solutions is made up of equal concentrations of the acid and the conjugate base, then



Equation 2 can be written as

$$[\text{H}^+] = K_a \times 1$$

Thus

$$[\text{H}^+] = K_a$$

Since

$$\text{pH} = -\log_{10} [\text{H}^+]$$

Then

$$\begin{aligned}\text{pH} &= -\log_{10} (K_a) \quad (\text{since } [\text{H}^+] = K_a) \\ &= \text{p}K_a\end{aligned}$$

Hence if a buffer solution is made by mixing equal concentrations of the weak acid and its salt then the pH is equal to the $\text{p}K_a$ of the weak acid.

Henderson-Hasselbalch equation

It is often convenient to relate the pH of a weak acid to the $\text{p}K_a$. Consider the reaction



The acid dissociation constant (K_a) would be

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

This equation can be rearranged to make the concentration of hydrogen ions the subject. Thus

$$[\text{H}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]}$$

Taking negative logarithms on both sides of the equation

$$\begin{aligned}\text{pH} &= -\log_{10} \frac{K_a[\text{HA}]}{[\text{A}^-]} \\ &= -\log_{10} K_a - \log_{10} \frac{[\text{HA}]}{[\text{A}^-]} \\ \text{pH} &= \text{p}K_a - \log_{10} \frac{[\text{HA}]}{[\text{A}^-]}\end{aligned}$$

or

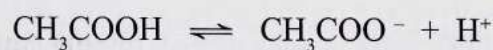
$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-] \text{ [salt]}}{[\text{HA}] \text{ [acid]}}$$



This is the well-known Henderson-Hasselbalch equation that is often used to perform the calculations required in preparation of buffers.

Example 1

- (a) What is the pH of a buffer solution made by making up 1 dm³ of solution containing 1 mol dm⁻³ CH₃COOH and 1 mol dm⁻³ CH₃COONa. K_a of ethanoic acid = 1.74 × 10⁻⁵ mol dm⁻³.
- (b) Calculate the change in pH when 0.1 mole of NaOH is added to this buffer. (Assume there is no change in volume)
- (a) Find H⁺ ion concentration



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

ethanoate ions from CH₃COONa

acid only slightly ionised

The [H⁺] is not equal to the [CH₃COO⁻]

Assumption: [CH₃COONa] = [CH₃COO⁻]

Therefore [CH₃COO⁻] = 1 mol dm⁻³

[CH₃COOH] = 1 mol dm⁻³

Thus

$$1.74 \times 10^{-5} = 1.00 [\text{H}^+]/1.00$$

$$[\text{H}^+] = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pH} = 4.76$$

The pH can also be calculated by substituting values in the Henderson-Hasselbalch equation

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log_{10} ([\text{A}^-] / [\text{HA}]) \\ &= 4.76 + \log_{10} (1/1) \\ &= 4.76\end{aligned}$$

- (b) On adding 0.1 mole NaOH, 0.1 mole of ethanoic acid reacts with the NaOH to form 0.1 mole of sodium ethanoate. Therefore the concentration of ethanoic acid decreases by 0.1 mole and the concentration of sodium ethanoate increases by 0.1 mole.

$$\begin{aligned}
 [\text{CH}_3\text{COOH}] &= 1 - 0.1 \\
 &= 0.9 \text{ mol dm}^{-3} \\
 [\text{CH}_3\text{COO}^-] &= 1 + 0.1 \\
 &= 1.1 \text{ mol dm}^{-3} \\
 1.74 \times 10^{-5} &= 1.1 [\text{H}^+]/0.9 \\
 [\text{H}^+] &= \frac{0.9 \times 1.74 \times 10^{-5}}{1.1} \\
 \text{pH} &= 4.85
 \end{aligned}$$

Or using the Henderson-Hasselbalch equation

$$\begin{aligned}
 \text{pH} &= \text{pK}_a + \log_{10} ([\text{A}^-] / [\text{HA}]) \\
 &= 4.76 + \log_{10} (1.1/0.9) \\
 &= 4.76 + 0.09 \\
 &= 4.85
 \end{aligned}$$

The change in pH is 0.09 units.

Example 2

Calculate the pH of a buffer solution made by dissolving 18.5 g of propanoic acid ($\text{C}_2\text{H}_5\text{COOH}$) and 12.0 g of $\text{C}_2\text{H}_5\text{COONa}$ in water and then making the volume up to 250 cm^3 . $K_a = 1.35 \times 10^{-5} \text{ mol dm}^{-3}$.

1 mol of $\text{C}_2\text{H}_5\text{COOH} = 74 \text{ g}$, 1 mol of $\text{C}_2\text{H}_5\text{COONa} = 96 \text{ g}$

$$\text{molarity of propanoic acid} = \frac{18.5 \times 4}{74} = 1 \text{ mol dm}^{-3}$$

$$[\text{C}_2\text{H}_5\text{COONa}] = \frac{12 \times 4}{96} = 0.5 \text{ mol dm}^{-3}$$

Substituting values in the equilibrium expression

$$\begin{aligned}
 1.35 \times 10^{-5} &= \frac{0.5 \times [\text{H}^+]}{1} \\
 [\text{H}^+] &= 2.7 \times 10^{-5} \text{ mol dm}^{-3}
 \end{aligned}$$

Hence

$$\text{pH} = 4.57$$

Or using the Henderson-Hasselbalch equation

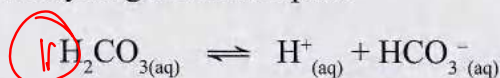
$$\begin{aligned}
 \text{pH} &= \text{pK}_a + \log_{10} ([\text{A}^-] / [\text{HA}]) \\
 &= 4.87 + \log_{10} (0.5/1) \\
 &= 4.87 - 0.30 \\
 &= 4.57
 \end{aligned}$$



Buffers in biological systems

The body maintains the pH of blood at about 7.4. If the pH level is not maintained, serious health consequences can result. A decrease in blood pH is called **acidosis** while an increase in blood pH is called **alkalosis**. Three main buffer systems in blood are the carbonic acid/hydrogencarbonate buffer, the phosphate buffer and the amino acid buffer.

In the carbonic acid/hydrogencarbonate buffer, the carbonic acid (H_2CO_3) is the hydrogen ion donor, hydrogencarbonate ion (HCO_3^-) is the hydrogen ion acceptor.

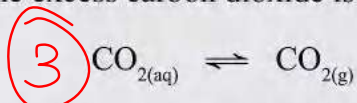


Additional H^+ is trapped by HCO_3^- ions and equilibrium shifts to the left. Additional OH^- is trapped by H^+ to form water and equilibrium shifts to the right to restore H^+ ions.

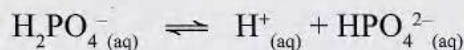
The carbonic acid concentration is controlled by respiration. Carbonic acid is in equilibrium with dissolved carbon dioxide gas.



An increase in dissolved carbon dioxide stimulates increased breathing and the excess carbon dioxide is exhaled by the lungs.



The phosphate buffer system consists of dihydrogen phosphate ions (H_2PO_4^-) as hydrogen ion donor (acid) and hydrogen phosphate ions (HPO_4^{2-}) as hydrogen ion acceptor (base). These two ions are in equilibrium with each other as indicated by the chemical equation below.



If acid is added to the system, the equilibrium shifts to the left. If hydroxide ions are added to the system, they react with H^+ ions to form water and the equilibrium shifts to the right to restore the H^+ ions.

The amino acid consists of the $-\text{COOH}$ group as the hydrogen ion donor and the $-\text{NH}_2$ group as the hydrogen ion acceptor. Amino acids exist as dipolar ions in aqueous solution called **zwitterions**.



Zwitterions can act as buffers in biological systems. If a bit of H^+ is added to an aqueous solution of amino acid, the zwitterion quickly accepts the H^+ protonating the COO^- group as shown in the equation below.

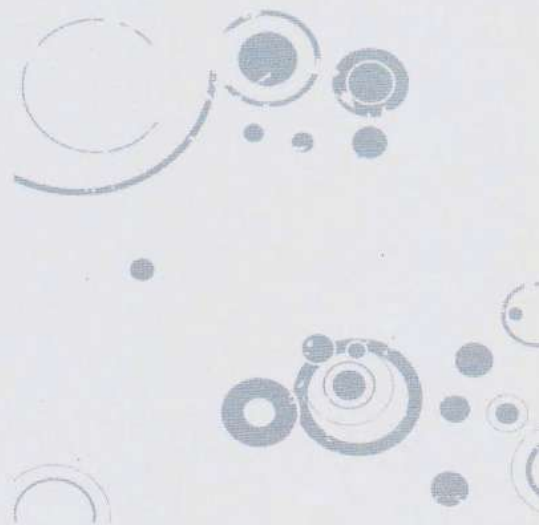


H^+ is removed thereby maintaining pH.

If a bit of OH^- ions are added, the NH_3^+ group quickly gives up an H^+ forming water as shown in the equation below.



The OH^- is removed thereby maintaining the pH of the solution.





Questions

- State what is meant by a buffer solution.
 - Give an example of a buffer solution.
 - Explain how the buffer solution named in (b) above resists changes in pH when an acid or alkali is added to it.

- A buffer solution was made by adding 6.56 g of sodium ethanoate to 1 dm³ of 0.02 mol dm⁻³ ethanoic acid.

- What is the concentration of the sodium ethanoate?
- What is the concentration of the ethanoic acid?
- Use the relationship

$$\text{pH} = \text{pK}_a - \lg [\text{acid}] / [\text{salt}]$$

to calculate the pH of the buffer solution.

$$(\text{K}_a \text{ CH}_3\text{COOH} = 1.8 \times 10^{-5} \text{ mol dm}^{-3})$$

- 0.002 g of solid sodium hydroxide was added to the buffer solution in question 2 above. Assuming that there was no change in volume, find the following:

- The new concentration of the sodium ethanoate.
- The new concentration of the ethanoic acid
- The change in pH of the buffer solution.

- Explain the following as fully as you can how:

- HCO_3^- (aq) helps to control the pH of blood.
- amino acids function as buffers in the blood.

Use equations to show how each system maintains the pH of the blood when an acid and an alkali is added.

- 1 dm³ of a solution contains 0.2 mole of ethanoic acid and 0.5 mole of sodium ethanoate.

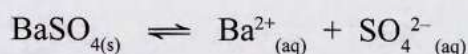
- Calculate the pH of the solution.

$$\text{pH} = \text{pK}_a - \lg [\text{acid}] / [\text{salt}] \quad \text{where } \text{pK}_a \text{ is } 4.76$$

- What is the change in pH when 0.005 mole of HCl is added?
- What is the change in pH when 0.005 mole of NaOH is added?



Many salts which we refer to as insoluble do actually dissolve to a small extent. The term sparingly soluble is usually used for these types of salts. In a saturated solution of a sparingly soluble salt, equilibrium can be established between dissolved ions and undissolved salt at a given temperature. Consider the following example at 25°C



We can write an equilibrium expression as

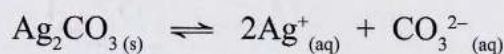
$$K_c = \frac{[\text{Ba}^{2+}_{(aq)}][\text{SO}_4^{2-}_{(aq)}]}{[\text{BaSO}_{4(s)}]}$$

Since only a very small amount of $\text{BaSO}_{4(s)}$ dissolves and its concentration is in large excess, the concentration of $\text{BaSO}_{4(s)}$ remains relatively constant. Thus cross-multiplying gives

$$K_c [\text{BaSO}_{4(s)}] = [\text{Ba}^{2+}_{(aq)}][\text{SO}_4^{2-}_{(aq)}]$$

A constant K_c multiplied by a constant (the concentration of $\text{BaSO}_{4(s)}$) gives a new constant which we call the **solubility product (K_{sp})**. Thus the solubility product of $\text{BaSO}_{4(s)}$ at 25°C is the product of the concentration of the cation and anion in a saturated solution. Like other equilibrium constants, solubility product varies with temperature.

Consider the another example



$$K_c = \frac{[\text{Ag}^{+}_{(aq)}]^2 [\text{CO}_3^{2-}_{(aq)}]}{[\text{Ag}_2\text{CO}_{3(s)}]}$$

$$K_c [\text{Ag}_2\text{CO}_{3(s)}] = [\text{Ag}^{+}_{(aq)}]^2 [\text{CO}_3^{2-}_{(aq)}]$$

$$K_{sp} = [\text{Ag}^{+}]^2 [\text{CO}_3^{2-}]$$

Notice the squared term of the concentration is on the silver ions. The stoichiometry must be taken into consideration for K_{sp} . Thus **the solubility product of a sparingly soluble salt can be defined as the product of the concentrations of the ions in a saturated**

solution of the salt, raised to the appropriate powers.



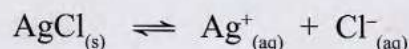
SOLUBILITY AND THE SOLUBILITY PRODUCT

Solubility product can be calculated from the solubility of a salt.

Example 1

If the solubility of $\text{AgCl}_{(s)}$ at 18°C is $1.00 \times 10^{-5} \text{ mol dm}^{-3}$, calculate a value for K_{sp} at this temperature.

The solubility means that 1×10^{-5} mole of AgCl is dissolved in 1 dm^3 of water at equilibrium. From the equation



$1 \times 10^{-5} \text{ mol dm}^{-3} \text{ AgCl}_{(s)}$ would form $1 \times 10^{-5} \text{ mol dm}^{-3} \text{ Ag}^+$ ions and $1 \times 10^{-5} \text{ mol dm}^{-3} \text{ Cl}^-$ ions.

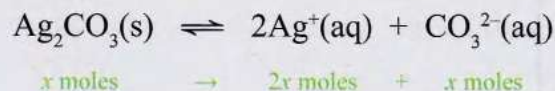
$$\begin{aligned} K_{sp} &= [\text{Ag}^+] [\text{Cl}^-] \\ &= [1 \times 10^{-5} \text{ mol dm}^{-3}] [1 \times 10^{-5} \text{ mol dm}^{-3}] \\ &= 1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6} \end{aligned}$$

Example 2

If the solubility product of silver carbonate at 20°C is $8 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$, calculate the solubility of the Ag_2CO_3 .

Let solubility of the Ag_2CO_3 be x , that is, x moles of Ag_2CO_3 is dissolved in 1 dm^3 of water at equilibrium.

From the equation



$$\begin{aligned} K_{sp} &= [\text{Ag}^+_{(aq)}]^2 [\text{CO}_3^{2-}_{(aq)}] \\ &= (2x)^2 (x) \\ &= 4x^3 \end{aligned}$$

Thus

$$\begin{aligned} 4x^3 &= 8 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9} \\ x &= 1.26 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

Therefore the solubility of silver carbonate at 20°C is $1.26 \times 10^{-4} \text{ mol dm}^{-3}$.



Example 3

Calculate the solubility of AgCl in a solution of 0.1 mol dm^{-3} hydrochloric acid at 18°C .

$$K_{\text{sp}} = 1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

Since hydrochloric acid is fully ionised and little dissociation occurs with AgCl, the Cl^- ions from AgCl is neglected.

$$\therefore [\text{Cl}^-] = 0.1 \text{ mol dm}^{-3}$$

$$\text{So } 1 \times 10^{-10} = [\text{Ag}^+][0.1]$$

$$[\text{Ag}^+] = 1 \times 10^{-9} \text{ mol dm}^{-3}$$

Thus the solubility of AgCl decreases in 0.1 mol dm^{-3} hydrochloric acid.

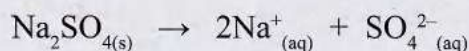
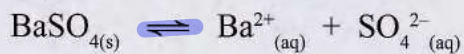
Limitations of K_{sp}

- K_{sp} is valid only for saturated solutions in which the concentration of the ions is no more than 0.01 mol dm^{-3} .
- K_{sp} is affected by temperature since it is an equilibrium constant.

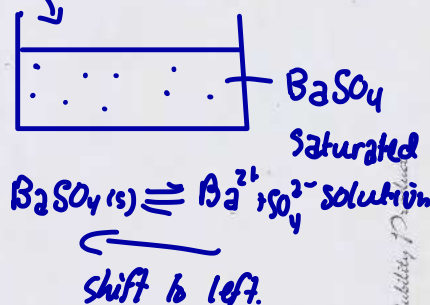
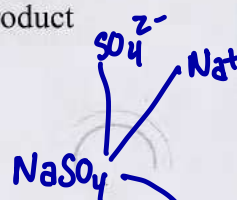


THE COMMON ION EFFECT

This is simple application of Le Chatelier's principle. If some sodium sulphate is added to a saturated solution of $\text{BaSO}_4(\text{s})$, the equilibrium system would be disrupted but the solubility product (K_{sp}) would remain the same.



The presence of the sodium sulphate increases the concentration of SO_4^{2-} ions in the mixture. An increase in the concentration of SO_4^{2-} ions would cause a decrease in concentration of Ba^{2+} ions to keep the solubility product at a constant value. Thus the equilibrium shifts to the left and reduces the solubility of BaSO_4 . The addition of the sulphate ions results in the precipitation of solid BaSO_4 . The precipitation of a solute on addition of another solution which has an ion in common with the solute is referred to as the **common ion effect**.





PREDICTING PRECIPITATION

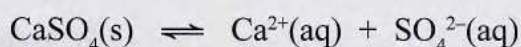
Precipitation of a sparingly soluble salt on addition of another solution which has an ion in common with the salt occurs only if the ionic product of the solution at that moment exceeds the solubility product. To predict whether precipitation of a salt will occur when a solution with a common ion is added, we can compare the ionic product of the solution upon mixing to the solubility product.

- If the ionic product $< K_{sp}$, then no precipitation occurs
- If the ionic product $= K_{sp}$, then a saturated solution forms
- If the ionic product $> K_{sp}$, then precipitation occurs.

Consider the following examples:

Example 1

Determine if a precipitate will form when a solution of calcium sulphate containing $5 \times 10^{-4} \text{ mol dm}^{-3}$ of Ca^{2+} ions is mixed with an equal volume of a solution of $5 \times 10^{-4} \text{ mol dm}^{-3}$ SO_4^{2-} ions at 25°C . The solubility product of CaSO_4 is $2.4 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$ at 25°C .



$$\begin{aligned} K_{sp} &= [\text{Ca}^{2+}_{(\text{aq})}] [\text{SO}_4^{2-}_{(\text{aq})}] \\ &= 2.4 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6} \end{aligned}$$

Upon mixing and before any precipitation occurs, the $[\text{Ca}^{2+}_{(\text{aq})}]$ is halved since 5×10^{-4} mole of Ca^{2+} is now present in 2 dm^3 of solution. The $[\text{SO}_4^{2-}_{(\text{aq})}]$ remains the same since twice the number of moles is in 2 dm^3 of solution.

$$[\text{Ca}^{2+}_{(\text{aq})}] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{SO}_4^{2-}_{(\text{aq})}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{The ionic product upon mixing} &= [\text{Ca}^{2+}] [\text{SO}_4^{2-}] \\ &= (2.5 \times 10^{-4}) (5 \times 10^{-4}) \\ &= 1.25 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6} \end{aligned}$$

Since $K_{sp} = 2.4 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$, the ionic product upon mixing is less than the solubility product (K_{sp}) therefore no precipitation occurs.



Example 2

Will a precipitate form when a solution of calcium sulphate containing $5 \times 10^{-2} \text{ mol dm}^{-3}$ of Ca^{2+} ions is mixed with an equal volume of a solution of $5 \times 10^{-2} \text{ mol dm}^{-3}$ SO_4^{2-} ions at 25°C .

$$[\text{Ca}^{2+}_{(\text{aq})}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$$

$$[\text{SO}_4^{2-}_{(\text{aq})}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\begin{aligned}\text{The ionic product upon mixing} &= [\text{Ca}^{2+}] [\text{SO}_4^{2-}] \\ &= (2.5 \times 10^{-2}) (5 \times 10^{-2}) \\ &= 1.25 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6}\end{aligned}$$

Since $K_{\text{sp}} = 2.4 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$, the ionic product upon mixing exceeds the solubility product (K_{sp}) therefore precipitation occurs. Equilibrium shifts to the left to decrease the concentration of ions in solution so that the ionic product becomes equal to the solubility product. Precipitation occurs to restore equilibrium to the system.



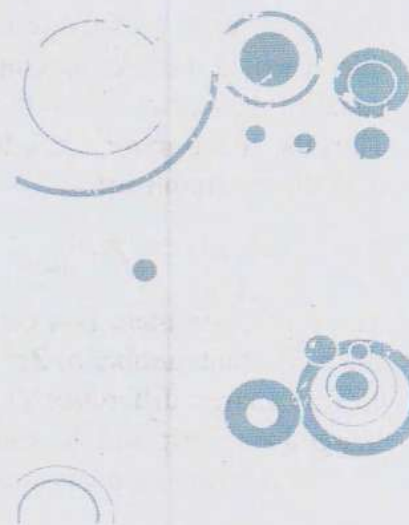


Questions

1.
 - (a) With reference to lead (II) iodide, explain the meaning of the term *solubility product* (K_{sp}) of a sparingly soluble salt.
 - (b) What is the units of the K_{sp} of lead (II) iodide?
 - (c) The solubility product of lead (II) iodide is $1.4 \times 10^{-8} \text{ mol}^3 \text{ dm}^{-9}$ at 25°C , calculate the solubility of lead (II) iodide at 25°C .
2. Although Ba^{2+} ions are toxic, a suspension of BaSO_4 can be swallowed as a 'barium meal' to investigate gastrointestinal problems since the solubility of BaSO_4 is very low. Given the molar solubility of BaSO_4 is 2.2×10^{-3} at 25°C , calculate the solubility product of BaSO_4 at 25°C .
3. A saturated solution of barium sulphate is made at 25°C and the mixture is filtered. Explain how each of the following is affected if a few drops of 1 mol dm^{-3} sodium sulphate is added to the filtrate:
 - (a) The solubility of BaSO_4
 - (b) The K_{sp} of BaSO_4
4. The molar solubility of lead (II) chloride is $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ at 298K .
 - (a) Write an expression for the solubility product of lead (II) chloride.
 - (b) Calculate the solubility product of lead (II) chloride.
 - (c) When a little concentrated sodium chloride solution is added to the filtrate of a saturated solution of lead (II) chloride, a white precipitate is formed. Explain this observation.
 - (d) How does an increase in temperature affect the solubility product?



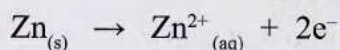
5. Calcium fluoride is used as a source of low concentration of fluoride ions in toothpaste. Since Ca^{2+} ions strengthen the teeth, it is suggested to add CaCl_2 to toothpaste to enhance its performance.
- Given the K_{sp} of CaF_2 is $4 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$, calculate the solubility of calcium fluoride.
 - Calculate the solubility of calcium fluoride in a solution of CaCl_2 of concentration 0.02 mol dm^{-3} .
 - Comment on the suggestion to add CaCl_2 to enhance the performance of the toothpaste.
6. In an experiment to determine the solubility product of calcium hydroxide, a saturated solution of calcium hydroxide was made at room temperature and filtered into a clean dry container. 25 cm^3 of the filtrate was pipetted into a conical flask and screened methyl orange indicator was added. The solution required 22 cm^3 of 0.05 mol dm^{-3} hydrochloric acid for neutralization. Explain how the titration results can be used to calculate a value for the solubility product of calcium hydroxide at the temperature of the experiment.



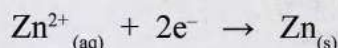


ELECTRODE POTENTIAL

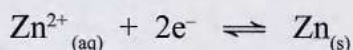
Redox reactions are reactions that involve the transfer of electrons between species. For example, if a strip of zinc is placed in a solution of its ions, the zinc metal loses electrons to form Zn^{2+} ions.



The electrons stay on the surface of the metal which becomes negatively charged. The Zn^{2+} ions in solution may then accept electrons from the surface of the metal and be discharged as zinc atoms.



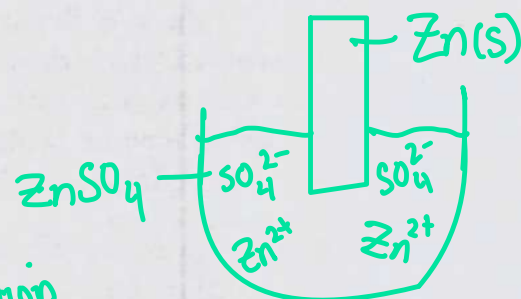
In the reaction, a dynamic equilibrium is established when the rate at which ions are leaving the surface of the metal is exactly equal to the rate at which they are being discharged on it again. Thus the equation for the redox reaction at equilibrium is written with the reversible arrow.



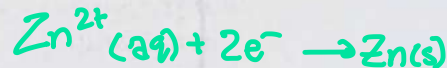
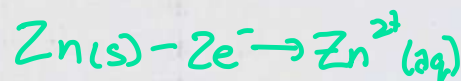
At equilibrium there is a constant negative charge on the zinc, and a constant number of Zn^{2+} ions present in the solution around it. This charge difference that develops between the negatively charged zinc strip and the solution is called a potential difference (we say the zinc strip has a **negative potential**).

► Fig. 12.1

A less reactive metal does not form ions readily. It can develop a positive potential if equilibrium is established in the direction where the metal ions in solution take electrons from the metal strip to form metal atoms. For example, if a strip of copper is placed into a solution of copper (II) sulphate, the copper develops a positive potential. The Cu^{2+} ions in the solution accept electrons from the copper strip since there is a greater tendency for the Cu^{2+} ions to reform Cu atoms. The electrons leave the copper strip giving it a **positive potential**.



Oxidation



Reduction

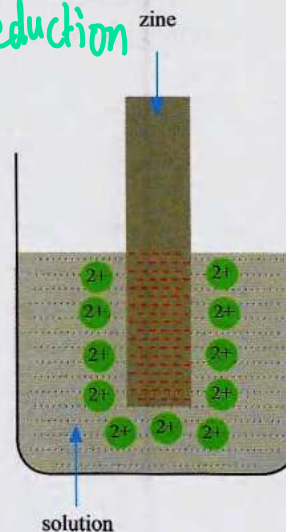


Fig. 12.1

Zn in a solution of Zn^{2+} ions

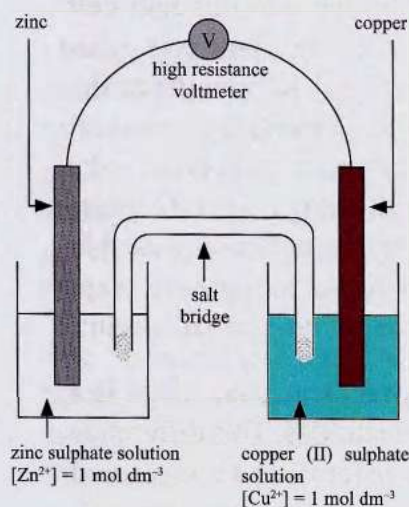
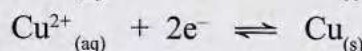
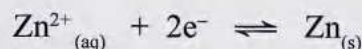


Fig. 12.2

A zinc-copper electrochemical cell

The potential difference between a metal and a solution of its ions depends on the nature of the metal and the concentration of the ions in the solution at equilibrium. Zinc has a more negative potential than copper since it tends to form ions more readily than copper. Using the equations below, we say that the equilibrium for the zinc reaction lies further to the left than the equilibrium for the copper reaction.

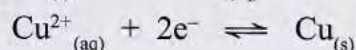
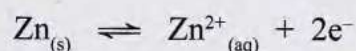


By convention, the electrons are written on the left-hand side of the equation for redox equilibria.

A metal immersed in a solution of its metal ions is called a **half-cell**. It is possible to combine two half-cells to form an electrochemical cell. An electrochemical cell is a type of cell in which a chemical reaction generates an electric current. The arrangement of an electrochemical cell is shown in Fig 12.2

Fig. 12.2

It consists of a zinc half-cell and a copper half-cell connected by an external wire, a voltmeter and a salt bridge. Cells are usually drawn with the more negative electrode on the left hand side. Since the Zn has a more negative potential than the Cu, the electrons flow through the external circuit from Zn to Cu. The Zn electrode dissolves in solution and Cu is deposited on the Cu electrode. Therefore the electrode reactions are

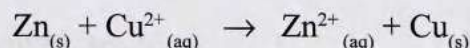


Oxidation occurs at the anode therefore the zinc electrode is the anode.

Reduction occurs at the cathode therefore the copper electrode is the cathode.

The electrons flow through the external circuit from the more negative electrode to the less negative electrode.

The overall cell reaction is

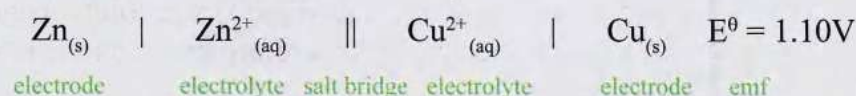


A **salt bridge** completes the circuit without allowing the two solutions to mix. It allows the migration of ions in both directions

to maintain electrical neutrality. A salt bridge may consist of a piece of filter paper soaked in saturated potassium nitrate solution or it may consist of a glass shaped U tube filled with agar jelly saturated with potassium chloride. When a half-cell loses electrons, positive charges build up in the half-cell. The NO_3^- or Cl^- ions migrate from the salt bridge into this half-cell to maintain electrical neutrality. When the other half-cell gains electrons, it becomes negatively charged and K^+ ions from the salt bridge neutralize this build up of negative charges. Potassium nitrate, potassium chloride and sodium chloride are suitable salts that can be used in construction of a salt bridge since they are very soluble and does not react with other ions commonly used in electrochemical cells. It is important to note that ions pass through the salt bridge while electrons move through the external circuit.

A flow of electrons in the external circuit indicates that there is a difference in potential between the two electrodes. This difference in potential is called an **electromotive force (emf)** and is measured in volts. A high resistance voltmeter is used to measure the emf. It uses negligible current therefore registering the maximum potential difference. The emf of the zinc/copper cell is 1.10 volts under standard conditions. Standard conditions are 25°C and 1 mol dm^{-3} solutions.

The half-cells and the emf of the electrochemical cell can be represented as shown below.



By convention, the half-cell in which oxidation occurs is written first.



THE STANDARD HYDROGEN ELECTRODE

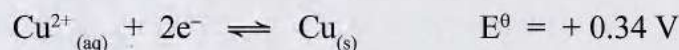
The potential difference or emf of a cell is the difference in potential of the two half-cells. The electrode potential of a single half-cell cannot be measured by itself. However, if we assign an electrode potential of a half-cell with an arbitrary value of zero, the electrode potential of other half-cells can be measured with reference to this standard.

The **standard hydrogen half-cell** also called the **standard hydrogen electrode** is used as the reference half-cell and is assigned a potential of zero volts. It consists of hydrogen gas

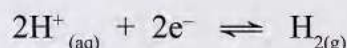


$\text{Cu}^{2+}_{(\text{aq})}/\text{Cu}_{(\text{s})}$ half-cell. Thus the Cu electrode is positive.

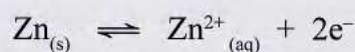
The voltmeter registers an emf of 0.34 volts. Since Cu is the positive terminal, the standard electrode potential for the $\text{Cu}^{2+}_{(\text{aq})}/\text{Cu}_{(\text{s})}$ half-cell is +0.34 volts. This is written as



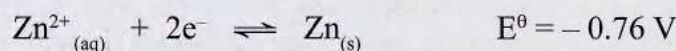
When the standard zinc half-cell is connected to the standard hydrogen electrode the voltmeter registers an emf of 0.76 volts. In this cell, the reactions at the electrodes are



and



The electrons flow from the $\text{Zn}^{2+}_{(\text{aq})}/\text{Zn}_{(\text{s})}$ half-cell to the standard hydrogen electrode. Thus the Zn electrode is negative. Since Zn is the negative terminal, the standard electrode potential for the $\text{Zn}^{2+}_{(\text{aq})}/\text{Zn}_{(\text{s})}$ half-cell is -0.76 volts. This is written as



When the standard hydrogen electrode is connected to the zinc half-cell the electrons flow in the opposite direction to that which occurs when it is connected to a copper half-cell.

Fig. 12.5

By convention, the hydrogen electrode is on the left hand side of the cell. This means that the sign of the standard electrode potential of a half-cell indicates whether that electrode is positive or negative.

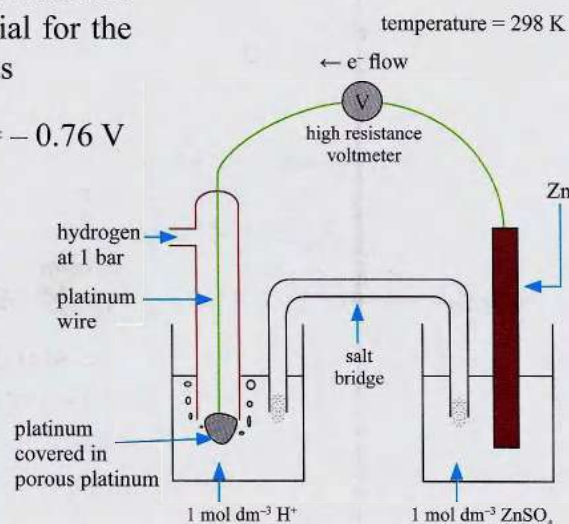


Fig. 12.5

Measuring the standard electrode potential of the zinc half cell

Measuring the $E^{\ominus}$ of half-cells involving no metals

Some redox systems do not involve metals but involve ions of the same element in different oxidation states. For such systems, a platinum electrode is immersed in a solution containing 1 mol dm^{-3} of both metal ions. For example, the $\text{Fe}^{3+}_{(\text{aq})}/\text{Fe}^{2+}_{(\text{aq})}$ half-cell is set up with a platinum electrode immersed in a solution containing 1 mol dm^{-3} Fe^{3+} ions and 1 mol dm^{-3} Fe^{2+} ions. The standard electrode potential of the $\text{Fe}^{3+}_{(\text{aq})}/\text{Fe}^{2+}_{(\text{aq})}$ half-cell can be measured by connecting it to a standard hydrogen electrode.

In redox systems that involve non-metals in contact with their aqueous ions, a platinum electrode is used. For example, the

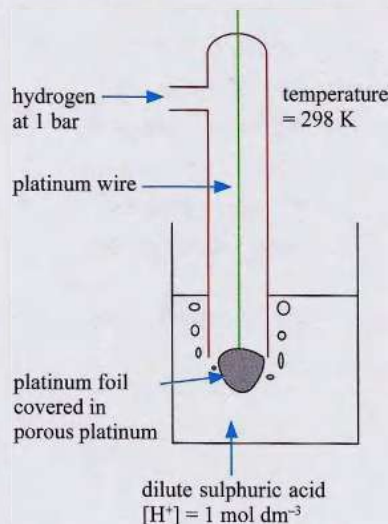


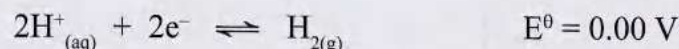
Fig. 12.3

The standard hydrogen electrode

bubbling over a platinum electrode immersed into a solution of H^+ ions under standard conditions. Standard conditions are:

- gases must be at 1 atm (101.3 kPa or 1 bar)
- the concentrations of the solutions must be 1 mol dm^{-3}
- the temperature must be 25°C (298K)
- Platinum is used as the electrode if a metal is not included in the half-cell.

Equilibrium is established between the hydrogen gas and the H^+ ions in the solution.



The platinum electrode is an inert electrode and does not form platinum ions. It consists of "platinized" platinum which catalyzes this reaction. Platinized platinum means that the Pt metal is coated with finely divided platinum to increase its surface area for equilibrium to be established in a relatively short time.

Fig. 12.3

The standard electrode potentials of other half-cells can be found by connecting them with the standard hydrogen electrode and measuring the potential difference of the cell.



STANDARD ELECTRODE POTENTIAL OF A CELL

The **standard electrode potential** (E^θ) of a standard half cell is the potential of that half-cell relative to a standard hydrogen electrode under standard conditions. The standard electrode potential of the $\text{Cu}^{2+}/\text{Cu}_{(\text{s})}$ half-cell is measured by connecting it to a standard hydrogen electrode as shown in Fig 12.4.

Fig. 12.4

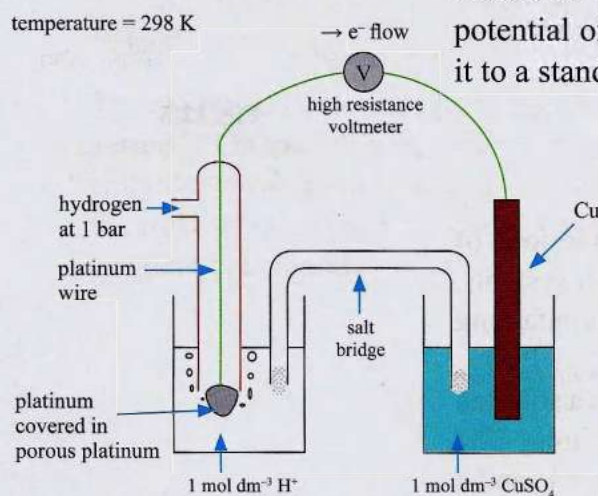
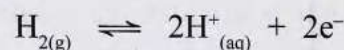


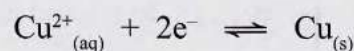
Fig. 12.4

Measuring the standard electrode potential of the copper half cell

The standard electrode potential of the $\text{Cu}^{2+}/\text{Cu}_{(\text{s})}$ half-cell is the potential difference between the standard hydrogen half-cell and the standard $\text{Cu}^{2+}/\text{Cu}_{(\text{s})}$ half-cell. In this cell, the reactions at the electrodes are



and



The electrons flow from the standard hydrogen electrode to the



$\text{Br}_{2(\text{aq})}/\text{Br}^{-}_{(\text{aq})}$ half-cell is set up with a platinum electrode immersed in a solution containing $1 \text{ mol dm}^{-3} \text{ Br}^{-}$ ions. The standard electrode potential of the $\text{Br}_{2(\text{aq})}/\text{Br}^{-}_{(\text{aq})}$ half-cell can be measured by connecting it to a standard hydrogen electrode. In a case where the half-cell involves a gas, for example, the $\text{Cl}_{2(\text{g})}/\text{Cl}^{-}_{(\text{aq})}$ half-cell, the half-cell consists of chlorine gas bubbling over a platinum electrode immersed into a solution of Cl^{-} ions under standard conditions.



USES OF STANDARD ELECTRODE POTENTIALS

To measure the relative strengths of oxidizing and reducing agents

The standard electrode potentials of redox systems are arranged in order of its values to give the electrochemical series. They give a measure of the relative oxidizing and reducing strengths of species. The standard electrode potentials of some redox systems are shown in the table below.

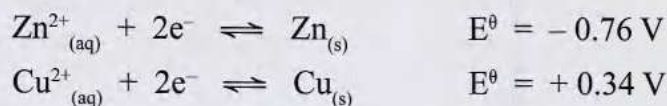
Table 12.1 Standard electrode potentials

Reactions	$E^{\ominus}/\text{V}$
$\text{K}^{+} + \text{e}^{-} \rightleftharpoons \text{K}$	-2.92
$\text{Ca}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Ca}$	-2.76
$\text{Na}^{+} + \text{e}^{-} \rightleftharpoons \text{Na}$	-2.71
$\text{Mg}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Mg}$	-2.37
$\text{Al}^{3+} + 3\text{e}^{-} \rightleftharpoons \text{Al}$	-1.66
$\text{Zn}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Zn}$	-0.76
$\text{Fe}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Fe}$	-0.44
$\text{Co}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Co}$	-0.28
$\text{Pb}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Pb}$	-0.13
$2\text{H}^{+} + 2\text{e}^{-} \rightleftharpoons \text{H}_2$	0.00
$\text{Sn}^{4+} + 2\text{e}^{-} \rightleftharpoons \text{Sn}^{2+}$	0.15
$\text{Cu}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Cu}$	0.34
$\text{I}_2 + 2\text{e}^{-} \rightleftharpoons 2\text{I}^{-}$	0.54
$\text{Fe}^{3+} + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}$	0.77
$\text{Ag}^{+} + \text{e}^{-} \rightleftharpoons \text{Ag}$	0.80
$\text{Br}_{2(\text{aq})} + 2\text{e}^{-} \rightleftharpoons 2\text{Br}^{-}$	1.07
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^{+} + 6\text{e}^{-} \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
$\text{Cl}_{2(\text{g})} + 2\text{e}^{-} \rightleftharpoons 2\text{Cl}^{-}$	1.36
$\text{MnO}_4^{-} + 8\text{H}^{+} + 5\text{e}^{-} \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.52
$\text{Au}^{+} + \text{e}^{-} \rightleftharpoons \text{Au}$	1.68
$\text{H}_2\text{O}_2 + 2\text{H}^{+} + 2\text{e}^{-} \rightleftharpoons 2\text{H}_2\text{O}$	1.77
$\text{F}_2(\text{g}) + 2\text{e}^{-} \rightleftharpoons 2\text{F}^{-}(\text{aq})$	2.87

**strongest
reducing
agent**



A negative value indicates that the species lose electrons more readily than hydrogen. This means it is a better reducing agent. A positive value means that the species gain electrons more readily than hydrogen. This means it is a better oxidizing agent than hydrogen. Using the following standard electrode potentials,

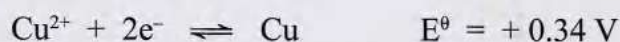


we can say that Zn is a stronger reducing agent than Cu while Cu^{2+} is a stronger oxidizing agent than Zn^{2+} . The stronger reducing agent has a more negative potential and the stronger oxidizing agent has more positive potential. Therefore standard electrode potentials can be used to predict the relative strengths of oxidizing and reducing agents.

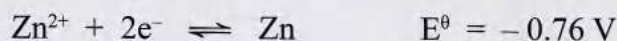
To calculate the standard cell potential

When two half-cells are connected under standard conditions, the maximum potential difference between the two half-cells is called the **standard cell potential**. The standard electrode potentials of the half-cells can be used to calculate the standard cell potential. For example, using the standard electrode potentials of the zinc and copper half-cells, the standard cell potential of the zinc/copper cell can be calculated as follows:

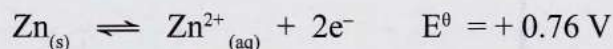
The standard electrode potential for the copper half-cell is



The standard electrode potential for the zinc half-cell is



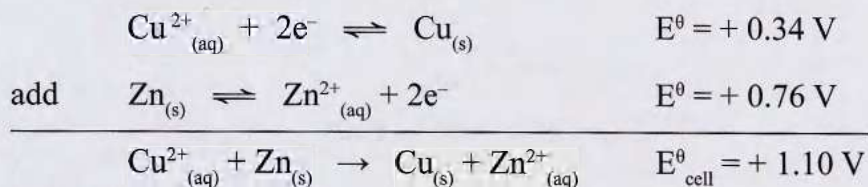
The $E^{\ominus}$ value that carries a more negative value is the negative electrode. In this case, zinc is the negative electrode while copper is the positive electrode. Electrons will therefore flow from the zinc half-cell to the copper half-cell. The equation for the reaction at the zinc electrode is in the reverse direction thus the sign of the $E^{\ominus}$ value changes. This is written as



The overall equation for the reaction can be written as



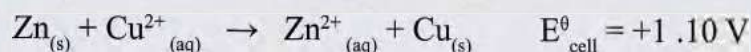
Hence the standard cell potential is



This means that the emf of an electrochemical cell can be calculated from the standard electrode potentials. The **Daniell cell** which has a similar arrangement to the zinc/copper cell has an emf of 1.10 volts. It was one of the first practical cells to be used.

To predict possible reactions

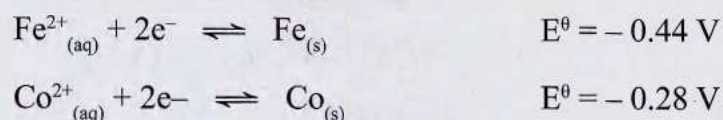
A reaction will only be feasible if the emf of the cell is positive. In the zinc/copper cell, the emf of the cell is +1.10 volts.



The overall positive potential of the cell suggests that the reaction is energetically feasible. This means that the Zn reduces Cu^{2+} to Cu while it was oxidized to Zn^{2+} . A negative emf implies that the reaction is non-feasible.

Consider a iron/cobalt half-cell.

Using standard electrode potentials



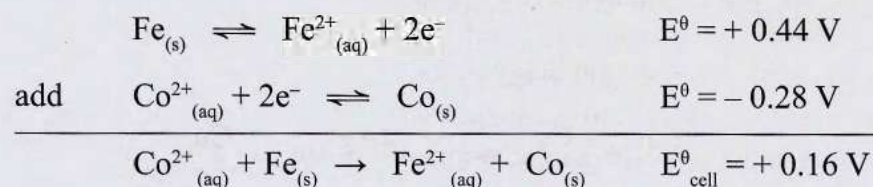
The standard electrode potential for iron is more negative therefore it is the negative electrode. The iron electrode loses electrons thus the sign of the E^{θ} value changes. This is written as



The overall equation for the reaction can be written as



Thus the standard cell potential is

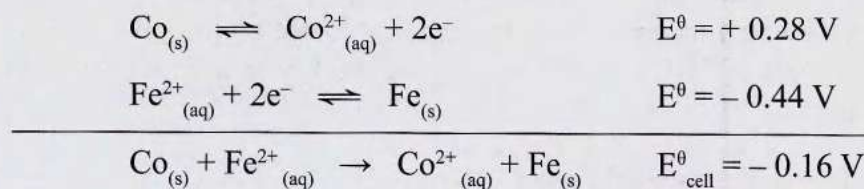


The reaction is energetically feasible since the overall emf is positive.

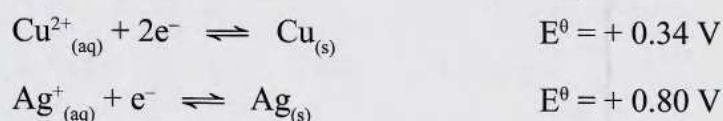
Compare the reaction below,



It will not be energetically feasible because the overall emf is negative as calculated below.



Consider a copper/silver cell.



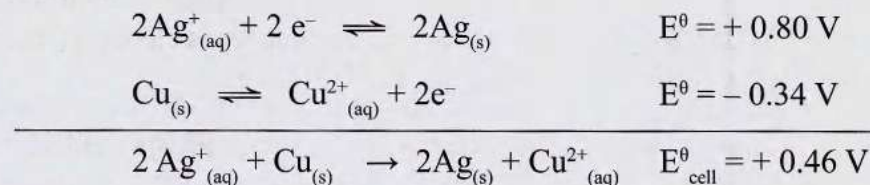
The standard electrode potential for copper is more negative (less positive) than that of silver therefore it is the negative electrode. The copper electrode loses electrons thus the reaction at the Cu electrode is



The overall equation for the reaction can be written as



Thus the standard cell potential is

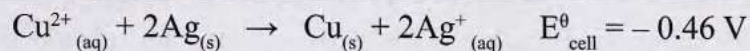
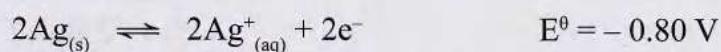


The positive emf value of +0.46 volts indicates the reaction is feasible. Note the silver equation is multiplied by 2 to balance the overall reaction however the E^{θ} value remains the same. E^{θ} values relate to the probability of a reaction occurring and not to the quantity of reacting species.

Compare the reaction below,



It will not be energetically feasible because the overall emf is negative as calculated below.



It is important to remember that the E^{θ} value indicates the feasibility of a reaction from an energetic point of view. It relates only to the relative stabilities of reactants and products however it gives no information about the rate of a reaction. Therefore it is possible for a reaction that is energetically feasible to be so slow that it appears not to occur, i.e. the rate is almost zero.



EFFECT OF CONCENTRATION ON ELECTRODE POTENTIAL

The values of standard electrode potentials are measured under standard conditions. However, changes in concentration, temperature and pressure will affect the values of electrode potentials. Standard temperature and pressure may be maintained but as soon as a reaction starts the concentration of reactants and products changes.

Consider the equilibrium between $\text{Cu}^{2+}_{(\text{aq})}$ and $\text{Cu}_{(\text{s})}$



If the concentration of the $\text{Cu}^{2+}_{(\text{aq})}$ decreases, then according to Le Chatelier's principle, the equilibrium would shift to the left producing more $\text{Cu}^{2+}_{(\text{aq})}$ and more electrons. Therefore the E^{θ} value of the half-cell would become more negative (less positive). The electrode potential of Cu immersed in $0.1 \text{ mol dm}^{-3} \text{ Cu}^{2+}$ solution is reduced to +0.31 volts.

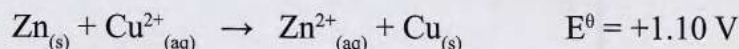
Consider the equilibrium between $\text{Zn}^{2+}_{(\text{aq})}$ and $\text{Zn}_{(\text{s})}$



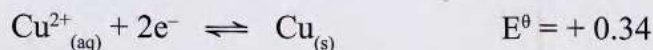
If the concentration of the $\text{Zn}^{2+}_{(\text{aq})}$ decreases, then according to Le Chatelier's principle, the equilibrium would shift to the left producing more $\text{Zn}^{2+}_{(\text{aq})}$ and more electrons. Hence the E^{θ} value of the half-cell would become more negative. The electrode potential of Zn in contact with $0.1 \text{ mol dm}^{-3} \text{ Zn}^{2+}$ solution is -0.79 volts.



Consider the overall reaction in the zinc/copper cell.



If the concentration of $\text{Cu}^{2+}_{(aq)}$ is increased, then according to Le Chatelier's principle equilibrium shifts to the right and the cell potential becomes more positive. As the concentration of $\text{Cu}^{2+}_{(aq)}$ increases, the E^θ value of the half-cell becomes more positive.



Thus the overall the E^θ value of the cell will increase.



ENERGY STORAGE DEVICES

Cells and batteries are useful and convenient energy storage devices. They convert chemical energy into electricity. A battery consists of two or more cells connected in series or parallel, but the term is sometimes used for single cells. Batteries which produce emf from irreversible chemical reactions are called **primary cells**. This means that when the chemicals in the cell are used up, the cell cannot be restored or recharged and must be discarded. Batteries which produce emf from reversible chemical reactions are called **secondary cells** or **accumulators**. In these batteries, the chemicals can be restored by passing an electric current through them in the opposite direction of normal cell operation.

The Daniell cell

The Daniell cell was one of the first practical cells to be used. It was invented in 1836 by John Frederic Daniell. It consists of a $\text{Zn}^{2+}_{(aq)}/\text{Zn}_{(s)}$ and a $\text{Cu}^{2+}_{(aq)}/\text{Cu}_{(s)}$ half-cell. Figure 12.6 shows a diagram of the Daniell cell.

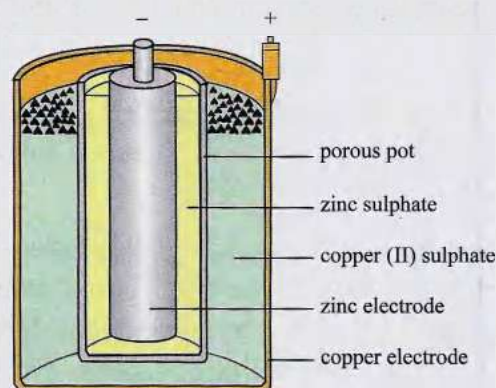


Fig. 12.6 A Daniell cell

The zinc anode is central and dips into a porous pot containing zinc sulphate solution. The porous pot is, in turn, immersed in a

copper pot containing copper (II) sulphate solution. The overall reaction in the cell is



The Daniell cell is a primary cell. The emf of the cell under standard conditions is 1.10 volts.

The dry Leclanché cell

The Leclanché cell was invented in 1867 by Georges Leclanché. In the dry Leclanché cell, the central carbon cathode is surrounded by a paste of manganese dioxide and carbon powder which increase the surface area of the positive terminal. This is, in turn, surrounded by a paste of zinc chloride and ammonium chloride dissolved in water. All is enclosed in a zinc case which serves as both a container and the anode.

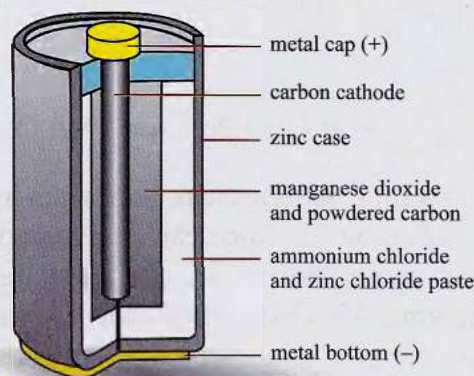
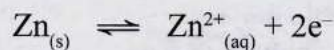
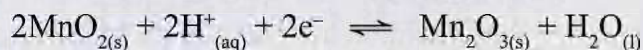


Fig. 12.7 The Leclanché cell

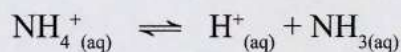
When the cell is in operation, the outer zinc case is oxidized according to the following half-equation:



At the cathode, the following reactions occur:



The H^{+} ions are provided by ammonium ions NH_4^{+} , through the reaction



The NH_3 then combines with the Zn^{2+} to form the complex ion, $[\text{Zn}(\text{NH}_3)_4]^{2+}$.

When the dry cell is used for some time, the zinc container becomes thinner as zinc case is oxidized to zinc ions. Thus the



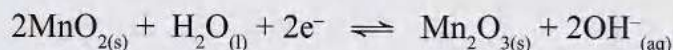
electrolyte leaks out the battery. Furthermore, the zinc casing gets thinner slowly even when the cell is not being used since the ammonium chloride inside the battery is acidic and reacts with the zinc. The dry Leclanché cell is a primary cell with a shelf life of around 1.5 years. The cell has an emf of about 1.5 V and is widely used as a source of electric energy in small appliances such as radios and torches.

Alkaline battery

Alkaline batteries are comparable to the dry Leclanché cell. The difference is that alkaline batteries use potassium hydroxide as an electrolyte instead of ammonium chloride or zinc chloride. The anode is made of zinc powder which increases the rate of reaction, while the cathode is made of manganese dioxide. The half-reactions are



and

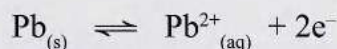


Over time, alkaline batteries leak potassium hydroxide which can cause skin irritation. Leakage can be avoided by using the same battery types in the same device and replacing all of the batteries at the same time. Also batteries should be removed from devices before storage.

Lead-acid accumulator

The lead-acid battery is a secondary cell which is charged before use. Once used, the battery can be recharged. It consists of three or six cells connected in series. Each cell produces an emf of about 2 volts. This provides 6 or 12 volts which generates enough electricity for starting an engine in a vehicle. Each cell consists of a lead anode and a lead (IV) oxide cathode immersed in concentrated sulphuric acid. When the cell is operating, the Pb anode dissolves to form Pb^{2+} ions and the PbO_2 cathode reacts with the H^{+} ions in the sulphuric to form Pb^{2+} ions.

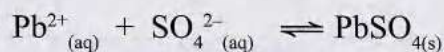
At the anode



At the cathode



The Pb^{2+} ions formed at the electrodes react with SO_4^{2-} ions in the acid to form insoluble lead (II) sulphate.



As the battery discharges, the concentration of sulphuric acid decreases and the electrodes are coated with a fine precipitate of lead (II) sulphate. This reduces the efficiency of the battery. However, when the vehicle is in operation, the alternator in the vehicle recharges the battery by passing an electric current through the battery in the opposite direction of the cell reactions. This reverses the cell reactions thus restoring the battery to its original condition. It must be noted that if discharge occurs for a long period of time, the PbSO_4 builds up and becomes coarser and inert. In this case, recharging the battery cannot restore it to its original condition. A lead-acid battery can be used for about four years.

The Fuel cell

Fuel cells are electrochemical cells that use fuels such as hydrogen, hydrocarbon or alcohol to produce electricity. It is a primary cell which differs from other electrochemical cells in that the fuel producing the electricity can be constantly replaced. Also the electrodes of the fuel cell are relatively inert and only catalyze the cell reactions. As long as the fuel is supplied, the fuel cell will continue to generate electricity.

The fuel cell in use today is the **hydrogen-oxygen fuel cell**. It consists of warm potassium hydroxide solution held between porous carbon electrodes as shown in the fig. 12.8 below. The electrodes are coated with a catalyst such as platinum or nickel which increases the rate of the cell reactions.

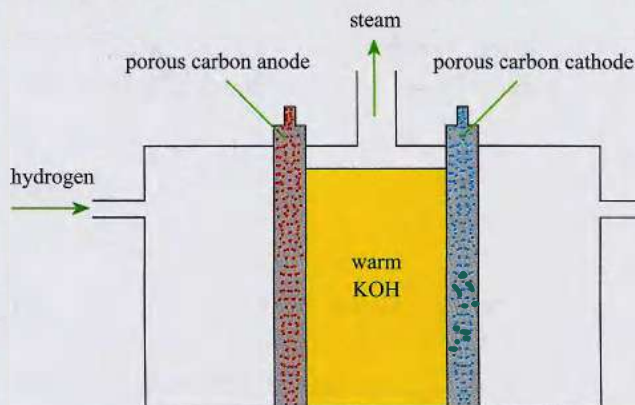


Fig. 12.8 The hydrogen-oxygen fuel cell

Hydrogen enters into the negative compartment of the cell and diffuses through the porous carbon anode. As hydrogen flows

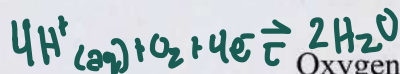
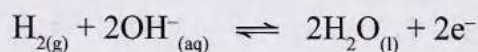
hydrogen bond.
Pure H_2 gas
really
explosive.



through the anode, the catalyst on the anode helps to separate the gas into hydrogen ions and electrons. The electrons flow through an external circuit while the hydrogen ions enter into the potassium hydroxide electrolyte. The hydrogen ions then combine with the hydroxide ions at the anode to form water.

cathode compartment

The overall reaction at the anode is

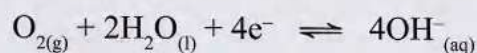


Oxygen enters into the positive compartment of the cell and diffuses through the porous carbon cathode into the potassium hydroxide. Oxygen, water and electrons catalytically combine to form hydroxide ions.

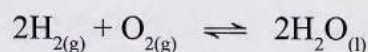
Overall rxn



Reaction at the cathode is



Combining both equations, the overall equation for the hydrogen-oxygen fuel cell is



what are the advantages

The hydrogen-oxygen fuel cell is highly efficient and pollution-free. They are used in spacecrafts to provide heat, electricity and drinking water for astronauts. The American Gemini Space probes and the Apollo Moon Vehicles used fuel cells. They are a promising technology for the future to use as fuel in vehicles and to provide power for homes and industries.





Questions

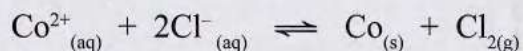
1. Define the following terms:
 - (a) standard hydrogen electrode
 - (b) standard electrode potential
 - (c) standard cell potential
2. Draw a labelled diagram to show how the standard electrode potential of a $\text{Zn}^{2+}_{(\text{aq})}/\text{Zn}_{(\text{s})}$ half-cell can be determined by connecting with the standard hydrogen electrode. Identify the cathode and anode in the diagram and indicate the direction in which the electrons flow through the external circuit.
3. A standard $\text{Zn}^{2+}_{(\text{aq})}/\text{Zn}_{(\text{s})}$ half-cell is connected to a standard $\text{Ag}^{+}_{(\text{aq})}/\text{Ag}_{(\text{s})}$ half-cell as shown below.



- (a) Draw a labelled diagram of the zinc-silver electrochemical cell.
 - (b) Write the equation for the reaction occurring at each electrode.
 - (c) Indicate the direction in which the electrons flow through the external circuit.
 - (d) Calculate the standard cell potential.
 - (e) Suggest how the cell potential would be affected if a solution of $0.1 \text{ mol dm}^{-3} \text{ Ag}^{+}$ ions was used instead of $1 \text{ mol dm}^{-3} \text{ Ag}^{+}$ ions. Explain your answer.
4. Draw a labelled diagram to show how the standard electrode potential of the following half-cells can be measured.
 - (a) $\text{Fe}^{3+}_{(\text{aq})}/\text{Fe}^{2+}_{(\text{aq})}$
 - (b) $\text{Cl}_{2(\text{g})}/\text{Cl}^{-}_{(\text{aq})}$
 - (c) $\text{Ag}^{+}_{(\text{aq})}/\text{Ag}_{(\text{s})}$
 5.
 - (a) Write a balanced equation for the reaction between aqueous Fe^{2+} ions and acidified dichromate ions.
 - (b) Calculate the emf of the cell in (a) above.



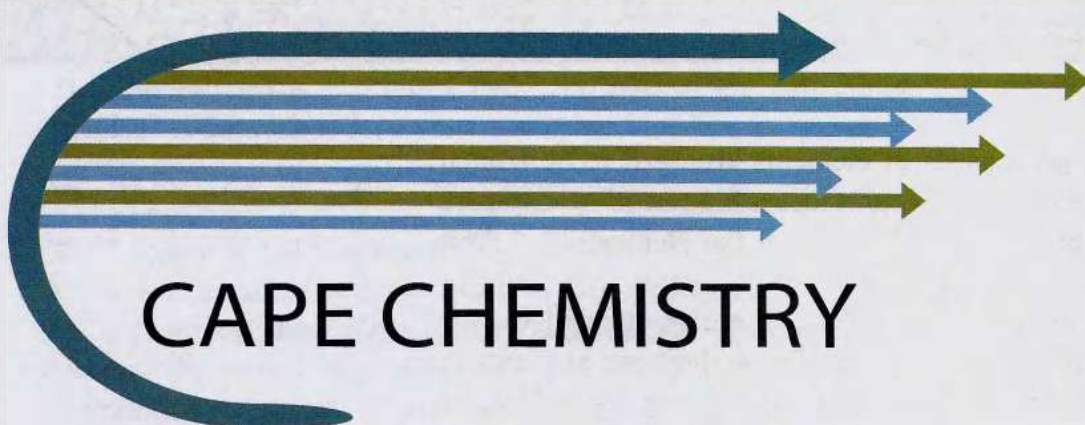
6. With reference to standard electrode potentials, discuss the possibility of the reaction below.



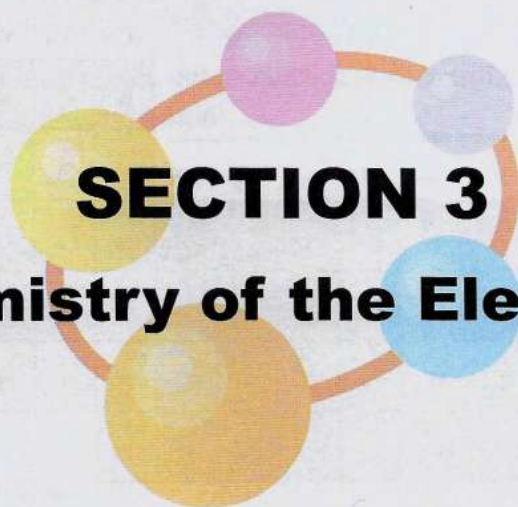
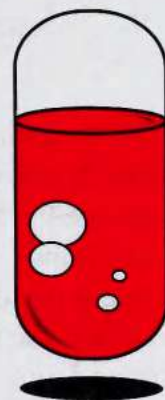
7. Fuel cells operate continuously as long as reactants are supplied. The hydrogen-oxygen fuel cell is used in spacecrafts to provide heat, electricity and drinking water for astronauts.
- With the aid of a labelled diagram identify the components of a hydrogen-oxygen fuel cell.
 - Write an equation for the reaction taking place at each electrode.
 - Write a balanced equation for the overall reaction.
 - Using standard electrode potential values, calculate the e.m.f. of the hydrogen-oxygen fuel cell.
 - Environmentalists suggest that the problem of air pollution can be greatly reduced by making use of fuel cells to provide electrical energy for industries.
 - Do you agree with this suggestion? Give a reason to support your answer.
 - Give one limitation to this suggestion.

8. Lead-acid batteries are used in automobiles.

- Identify the components of a lead-acid battery.
- Write an equation for the reaction taking place at each electrode during discharge.
- Calculate the standard cell potential.



CAPE CHEMISTRY



SECTION 3

Chemistry of the Elements

Patterns Across the Periodic Table

The Periodic Table consists of elements arranged in horizontal periods and vertical groups. It provides a framework to compare and predict the properties and trends of the elements and their compounds based on their location on the table. The periodic table is divided into four main blocks. These are the s block, the p block, the d block and the f block. The **s block** are elements in group I and II, the **p block** are elements in group III to VII and group 0, the **d block** are the transition metals and the **f block** are elements 57-71 and 89-103.

Different properties and trends are observed when moving vertically down a group or horizontally across a period. On moving across a period from left to right, the elements have the same number of electrons in the inner shells but the number of electrons on the valence shell increases. A new period starts when an electron enters a new shell. On moving down a group, the elements have the same number of valence electrons but the number of inner shells increases.

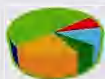
	1																	18	
	IA																	O	
1	1 H	2 He											13 B	14 C	15 N	16 O	17 F	2 He	
2	3 Li	4 Be		3	4	5	6	7	8	9	10	11	12					10 Ne	
			transition metals																
3	11 Na	12 Mg		IIIB	IVB	VB	VIB	VII	—	VII	—	IB	IIIB	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Rd	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110	111	112	113						

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Fig. 13.1

The periodic table. The recently proposed new numbering system for the groups is the red numbers 1-20.

The elements in the periodic table are divided into metals, metalloids and non-metals. The metals are on the left of elements shaded pink. Metalloids are shaded pink. Non-metals are on the right of elements shaded pink. The properties of the elements change on moving across a period. Some of these properties are highlighted as we look at some trends in period 3 elements, sodium to argon.



TRENDS IN PERIOD 3 ELEMENTS (Na TO Ar)

Variations in physical properties of the elements

In period 3 of the Periodic Table, the 3s and 3p orbitals are being filled with electrons.

The electronic structures for the eight elements are

Na	$1s^2 2s^2 2p^6 3s^1 3p^0$
Mg	$1s^2 2s^2 2p^6 3s^2 3p^0$
Al	$1s^2 2s^2 2p^6 3s^2 3p^1$
Si	$1s^2 2s^2 2p^6 3s^2 3p^2$
P	$1s^2 2s^2 2p^6 3s^2 3p^3$
S	$1s^2 2s^2 2p^6 3s^2 3p^4$
Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$
Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$

The elements have the same number of electrons in the inner shells but the number of electrons on the valence shell increases. These determine the structure and bonding of the elements which in turn relate to their properties.

Atomic radii

It is not possible to measure the radius of an isolated atom since the electron cloud of an atom has no definite boundary. The atom radius is found by measuring the distance between the nuclei of two identical atoms, and then halving that distance. The radius depends on the type of bonding that exists between the atoms. The covalent radius is measured for atoms which are covalently bonded to each other while the metallic radius is measured for atoms in a metallic structure. The noble gases which are not chemically bonded but held together by van der Waals forces, the van der Waals radius is measured. The van der Waals radius is larger than the covalent and metallic radii because the atoms are not held tightly together as seen in the noble gases.



The atomic radius of an atom is affected by the nuclear charge of the atom and the shielding effect of the inner electrons. As we move across period 3, the nuclear charge increases but the number of shells is the same. Thus there is a greater nuclear attraction for the same number of shells. This results in the outermost electron being more tightly held by the nucleus. Hence the radii of the atoms of period 3 decrease as we move across the period.

Fig. 13.2

Argon is not chemically bonded and is usually left out of the comparison.

Ionic radii

As the metallic character changes to non-metallic character across the period, the radius of the metallic ion is smaller than its corresponding atom while the radius of the non-metallic ion is larger than its corresponding atom.

Fig. 13.3

As we move across from sodium to aluminium in period 3, the ionic radius decreases. This is because the ratio of protons to electrons increases as the metal loses its outer shell of electrons. This increases the nuclear attraction on the remaining electrons. Thus the size of the metallic ion decreases.

As we move from phosphorous to chlorine in period 3, the ionic radius of the non-metallic ion is larger than its corresponding atom. This is because an additional electron is added to the valence shell which results in more electron repulsion. However, it must be noted that the ionic radius of phosphorous is larger than sulphur which is larger than chlorine. As the nuclear charge increases, the ionic radius of the negative ions of period 3 decreases.

Melting point

When investigating the melting point of a period 3 element, we ask three questions.

- What are the forces holding the solid state together? (metallic, covalent, ionic, intermolecular)
- Can these forces be broken down easily?
- Is the lattice stable?

As we move across the period from left to right, we observe that the melting point increases from the sodium to silicon and then



Fig. 13.2

Variation in atomic size

Na ⁺	Mg ²⁺	Al ³⁺	Si	P ³⁻	S ²⁻	Cl ⁻
0.095	0.065	0.05		0.212	0.184	0.181

Fig. 13.3

Variation in ionic size

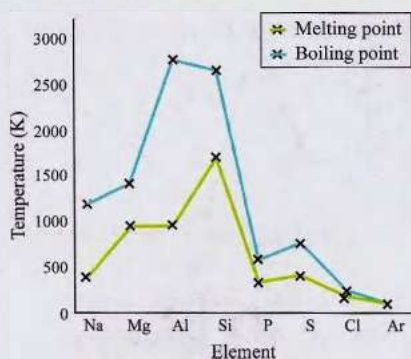


Fig. 13.4

The melting and boiling point of period 3 elements

the decreases from phosphorous to argon.

Fig. 13.4

Sodium, magnesium and aluminium are all metals. They have metallic bonding, in which positive metal ions are attracted to delocalized electrons. Moving from sodium to aluminium, the charge on the metal ions increases from +1 to +3 therefore the number of delocalized electrons increases. Thus the strength of the metallic bonding increases and the melting points and boiling points increase.

Silicon has giant molecular structure. It forms a giant lattice structure similar to that of diamond. Each silicon atom is covalently bonded to four other silicon atoms in a tetrahedral arrangement. This forms a three dimensional giant molecule. Silicon requires large amounts of energy to break its giant lattice. Thus it has a high melting and boiling point.

P, S and Cl exist as small discrete molecules held together by van der Waals forces of attraction. The melting points and boiling points are very low because van der Waals forces of attraction are very weak and not much energy is needed to overcome them.

The melting and boiling point of non-metals also depend on the size of the molecule. Generally, the larger the molecule, the greater the strength of the van der Waals forces of attraction. This explains why sulphur (which exists as S_8) has a higher melting point than P (which exists as P_4) which has a higher melting point than Cl (which exists as Cl_2).

Conductivity

For an element to be able to conduct electricity, mobile charge carriers must be present. In general, metals are good conductors of electricity while non-metals are poor conductors of electricity. Sodium, magnesium and aluminium are all metals. They are involved in metallic bonding, in which positive metal ions are attracted to delocalized electrons. The delocalized electrons are free to move and carry charge. Moving from sodium to aluminium, the number of delocalized electrons increases thus there are more charge carriers and the electrical conductivity increases.

The electrical conductivity then falls at silicon. Silicon is a metalloid, its four electrons are held strongly in covalent bonds. Few electrons have enough energy at room temperature to enter the higher energy levels. At higher temperatures, more electrons become delocalized and are available to carry charge.



The remaining elements phosphorus, sulphur, chlorine and argon are non metals and do not conduct electricity. In phosphorus, sulphur and chlorine, the electrons are held in covalent bonds and are not free to move and carry charge. Argon which exists as single atoms, the outer electrons are not free to move because they are held in a stable third energy level.

Fig. 13.5

Electrical conductivity increases going across period 3 from sodium to aluminium, then decreases to silicon. It further decreases to negligible conductivity in the remaining elements.

Electronegativity

Electronegativity measures the ability of an atom to attract the bonding electron pair in a covalent bond. Electronegativity cannot be measured directly but it can be measured relative to another atom. Fluorine is the most electronegative element and in the Pauling electronegativity index, it is given an electronegativity value of 4. The other elements are measured relative to this.

As we move across period 3, the nuclear charge increases while the atomic radius decreases. There are more electrons, but the shielding of inner electrons is negligible because each additional electron enters the same shell. Thus the effective nuclear attraction for the electrons increases hence the electronegativity increases across the period.

Fig. 13.6

Note that no values are given for argon as it does not usually form covalent bonds.

Density

The density of a substance is the ratio of the mass of a substance to its volume. For elements, this can be expressed in units of grams per cubic centimetre. The density of a pure substance varies little from sample to sample and is often considered a characteristic property of the substance. Most substances expand when heated and therefore have lower densities at higher temperatures. Many substances, especially gases, can be compressed into a smaller volume by increased pressure. Thus the temperature and pressure at which the density of a substance is measured are usually specified. The densities of period 3 elements are given in table 13.1.

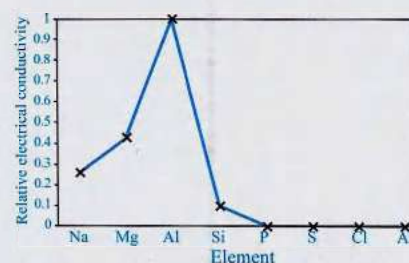


Fig. 13.5

The electrical conductivities of period 3 elements

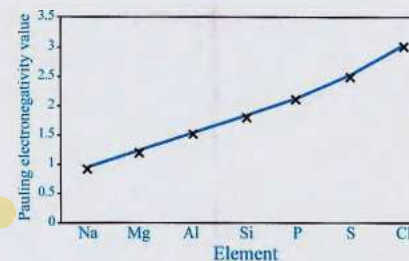


Fig. 13.6

The electronegativity values of period 3 elements

In the case of phosphorous, the three electrons in the 3p orbitals all have the same spin, but in sulphur the fourth electron is paired in one of the 3p orbitals.

P has the configuration $1s^2 2s^2 2p^6 3s^2 3p^3$

S has the configuration $1s^2 2s^2 2p^6 3s^2 3p^4$

The electron-electron repulsion in the paired 3p orbital makes it easier to remove the paired electron with opposite spin, thus the first ionization energy of sulphur is less than that of phosphorous.



SOME CHEMICAL REACTIONS OF PERIOD 3 ELEMENTS

As well as showing trends in physical properties, the elements in period 3 also show trends in chemical properties. Table 13.2 displays the reactions of the period 3 elements from sodium to argon with water, oxygen and chlorine.

Element	Reaction with oxygen	Reaction with chlorine	Reaction with water
Na	Burns vigorously to give both Na_2O and Na_2O_2	burns in chlorine with a bright orange flame to form NaCl	Violent reaction to form NaOH and H_2
Mg	Burns with a brilliant flame to form MgO	burns with a white flame to form MgCl_2	reacts with water to form Mg(OH)_2 and H_2 , reacts with steam to form MgO and H_2
Al	Burns to form a layer of Al_2O_3	Burns to form AlCl_3	Slow reaction with steam and powdered Al to form Al_2O_3 and H_2
Si	Burns at high temperatures to form SiO_2	Reacts with powder Si to form SiCl_4	No reaction
P	Burns vigorously to form P_4O_6 and P_4O_{10}	Burns in chlorine to produce PCl_3 and PCl_5	No reaction
S	Burns to form SO_2 and SO_3	Reacts to form S_2Cl_2	No reaction
Cl	No reaction	No reaction	Reacts to form HCl and HOCl
Ar	No reaction	No reaction	No reaction

Table 13.2

Reactions of period 3 elements with oxygen, chlorine and water





VARIATION IN OXIDATION STATES OF THE OXIDES AND CHLORIDES OF PERIOD 3 ELEMENTS

The formulae of the oxides and chlorides of period 3 elements show a pattern based on the elements highest oxidation state. The element highest oxidation state is equal to the number of electrons on the outer shell of the atom. This means that all the outer electrons in the period 3 element are involved in the bonding. Bonding occurs with just the one outer electron on sodium, to all seven outer electrons on chlorine.

Table 13.3

(a) Oxidation states of the oxides of period 3

Oxides	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀	SO ₃	Cl ₂ O ₇
Oxidation state of period 3 element	+1	+2	+3	+4	+5	+6	+7

(b) Oxidation states of the chlorides of period 3

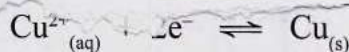
Chlorides	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₅
Oxidation state of period 3 element	+1	+2	+3	+4	+5

The highest oxidation state for the chloride of sulphur is in SCl₄. Sulphur does not form the hexachloride, possibly due to the atom not being able to accommodate more than four chlorine atoms around it. SCl₄ is unstable and readily decomposes to form S₂Cl₂.



PROPERTIES OF THE OXIDES AND CHLORIDES OF PERIOD 3

The oxides and chlorides show patterns in their properties across period 3. On the left hand side of the period, both the oxides and chlorides show properties typical of ionic compounds. Moving to the right of the period, the properties change to those typical of covalent compounds.



the standard hydrogen electrode to the

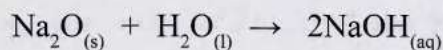


Table 13.4

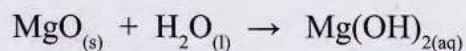
Some properties of the oxides of period 3 elements

Oxides	Bonding	Melting and boiling points	Reaction with water	Acid-base nature of oxide	pH
Na ₂ O	Ionic	High	Soluble, reacts to form NaOH	Basic	13
MgO	Ionic	High	Slightly soluble, reacts to form Mg(OH) ₂	Basic	11
Al ₂ O ₃	Ionic with covalent character	High	No reaction	Amphoteric	---
SiO ₂	Giant covalent	High	No reaction	Acidic	---
P ₄ O ₁₀	Simple covalent	Low	Vigorous reaction to form H ₃ PO ₄	Acidic	3
SO ₃	Simple covalent	Low	Vigorous reaction to form H ₂ SO ₄	Acidic	2
Cl ₂ O ₇	Simple covalent	Low	Vigorous reaction to form HClO ₄	acidic	2

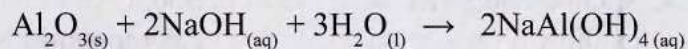
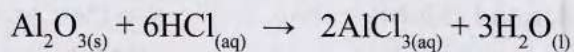
Na₂O dissolves readily in water to form an alkaline solution.



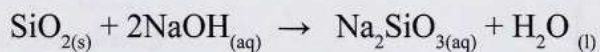
MgO is only slightly soluble in water to form an alkaline solution.



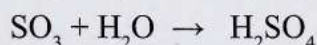
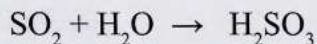
Al₂O₃ does not dissolve in H₂O. It is, however, amphoteric i.e. it has both acidic and basic properties.

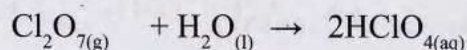
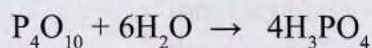
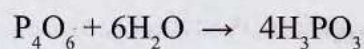


SiO₂ is insoluble in water but it reacts with hot concentrated alkali to form silicates.



Oxides of sulphur, phosphorous and chlorine react readily with water to form acidic solutions.





Chlorine (VII) oxide

chloric (VII) acid

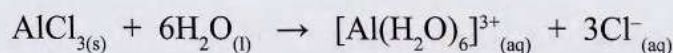
On moving across the period, the trend is from strongly basic oxides on the left-hand side to an amphoteric oxide in the middle to strongly acidic oxides on the right. These changes occur as the oxides change from metallic oxides which are bases to non-metallic oxides which are generally acidic. Thus the acid-base nature changes from basic to amphoteric to acidic on moving from left to right across the period.

The metallic oxides and silicon dioxide have high melting and boiling points because a lot of energy is needed to break the strong bonds that hold these three dimensional lattices together. The oxides of phosphorus, sulphur and chlorine consist of simple molecules held together by weak van der Waals forces. Therefore their melting and boiling points are low.

Table 13.5 Some properties of the chlorides of period 3 elements

Chlorides	Bonding	Melting and boiling points	Reaction with water	pH
NaCl	Ionic	High	Dissolves in water	7
MgCl ₂	Ionic	High	Dissolves in water	6.5
Al ₂ Cl ₆	Ionic with covalent character	Low	Reacts vigorously to form HCl fumes	3
SiCl ₄	Simple covalent	Low	Reacts vigorously to form HCl fumes	2
PCl ₅	Simple covalent	Low	Reacts vigorously to form HCl fumes	2
S ₂ Cl ₂	Simple covalent	Low	Vigorous reaction to form HCl	2
Cl ₂	Simple covalent	Low	Reacts to form HCl and HOCl	2

NaCl and MgCl₂ dissolve in water to form aqueous ions. The aluminium chloride reacts with the water rather than just dissolving in it. First it dissolves in water to form the hexaaquaaluminium ion and chloride ion.



Since the Al³⁺ ion is relatively small and highly charged, it draws

the electron density away from the water molecules in the complex ion causing them to give up H^+ ions.



Thus aluminium chloride is acidic in water.

The non-metal chlorides react with water to form acids.



Sodium and magnesium chlorides are ionic solids and require a large amount of heat to break the strong ionic attractions. These solids thus have high melting and boiling points. The other chlorides have low melting points. They form simple molecular structures with weak intermolecular forces of attractions.

The oxides and the chloride of the period 3 elements show a change from ionic to covalent bonding in their compounds on moving across the period from left to right. The change from ionic to covalent character can be related to increase in electronegativity across the period. Atoms of low electronegativity, like Na and Mg will give up electrons to atoms like oxygen and chlorine to form ionic compounds. Conversely, the more electronegative elements on the right of the period form covalent bonds with oxygen and chlorine.





Questions

1. Account for the variation of the following physical properties of the elements in period 3 in terms of structure and bonding:
 - (a) Atomic radii
 - (b) Melting point
 - (c) Electrical conductivity
 - (d) Electronegativity
 - (e) Density
2. Describe the reactions of the elements in period 3 with the following:
 - (a) oxygen
 - (b) chlorine
 - (c) water
3. Explain the variation in the oxidation number of the oxides of the period 3 elements.
4.
 - (a) Describe the trend in acid-base character of the oxides of period 3 elements.
 - (b) Aluminium oxide is described as an amphoteric oxide.
 - (i) What is an amphoteric oxide?
 - (ii) Illustrate the amphoteric nature of aluminum oxide with suitable chemical equations.
5.
 - (a) With reference to ionic radii and electronegativities, account for the type of chemical bonding present in the chlorides of period 3 elements.
 - (b) Describe the reactions of the chlorides of period 3 elements with water. Include equations where relevant.
 - (c) When aluminium chloride dissolves in water, its solution is acidic. Account for the acidic nature of the aluminium chloride solution.



The elements of group II are Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra). Beryllium does not follow the normal trend of the group II elements. Radium is radioactive and we do not look at its chemistry in analyzing group II. The focus is therefore on the elements Magnesium to Barium. This group is generally referred to as the 'alkaline earth metals'.



PHYSICAL PROPERTIES

The elements in group II show characteristic trends in physical properties on descending the group. Table 14.1 gives some properties of the group II elements.

Table 14.1 Some properties of group II elements.

Element	Atomic radius/nm	Ionic radius/nm	1 st ionization energy/kJ mol ⁻¹	Melting point/°C
Be	0.112	0.031	900	1280
Mg	0.160	0.065	736	650
Ca	0.197	0.099	590	850
Sr	0.215	0.113	548	768
Ba	0.217	0.135	502	714
Ra	0.220	0.140	510	700

Atomic radius

Atomic radius increases as we descend group II. This is expected as a fully filled orbital is added from one successive element to the next down the group. The primary screening effect also increases as these fully filled inner orbitals shields the outer electrons from the increasing nuclear charge. This results in the outer electrons being further from the nucleus causing an increase in the size of the atom. Although the proton number increases, the screening effect outweighs this increase in nuclear charge.



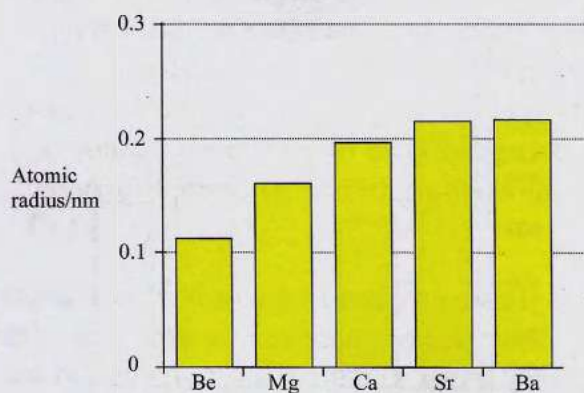


Fig. 14.1 Variation in atomic radius of group II

Ionization energy

First ionization energy is the energy needed for the complete removal of an electron from its outermost shell. Notice that first ionization energy decreases as you go down the group.

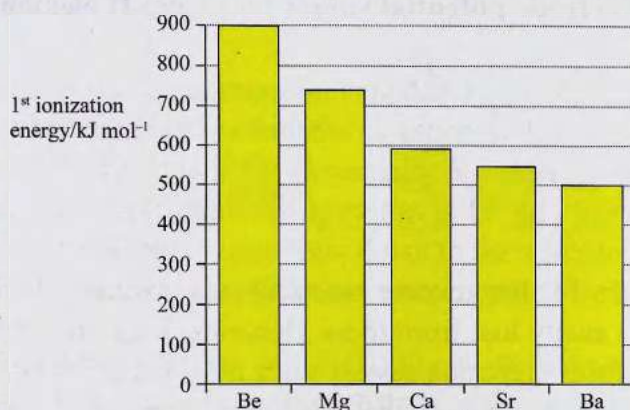


Fig. 14.2 Variation in 1st ionization energy of group II

Since the atomic radius increases down the group, the outer electrons get further away from the nucleus and less energy is required to remove an outer electron. Thus the ionization energy decreases down the group.

Melting point

With the exception of magnesium the melting point falls as you go down the group. The general decrease in melting point is explained in terms of the atomic and ionic radii. On moving down the group, the atomic and ionic radii increase and there is less attraction between the positive ions and the delocalized electrons in the metallic structure. Thus less energy is required to melt the structure.



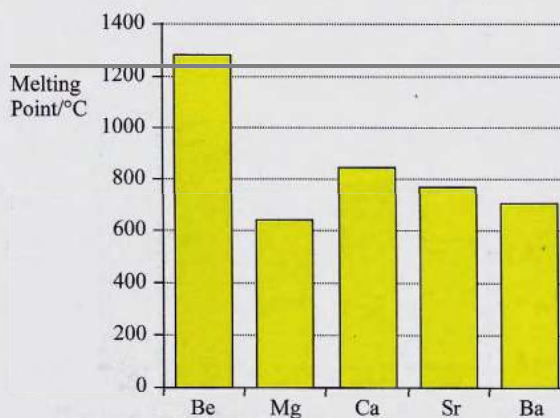


Fig. 14.3 Melting point of group II



CHEMICAL REACTIONS

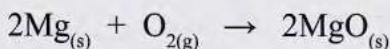
Standard electrode potential values for group II elements

Reaction	E^0/V	These values tell us the ease with which each reaction occurs. If the E^0 value is positive, the reaction is feasible
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.83	
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	-2.87	
$Sr^{2+} + 2e^- \rightleftharpoons Sr$	-2.89	
$Ba^{2+} + 2e^- \rightleftharpoons Ba$	-2.91	

All the values for the reverse reactions are positive, therefore, electrons are easily lost from these elements. It can be observed that barium loses electrons easiest since its value is 2.91V. From these values we can also see that reactivity increases as we move down the group.

Reactions with oxygen

All group II elements react with oxygen to form its metallic oxide. For example, Mg burns with a brilliant flame in oxygen to produce MgO.



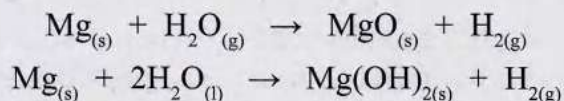
All burn readily in oxygen, reactions are highly exothermic and reactivity increases down the group. All of the group II metals tarnish in air as a layer of oxide is formed on the surface of the metal.

Reactions with water

Beryllium does not react with water while magnesium reacts slowly. Magnesium reacts rapidly with steam to form magnesium oxide and hydrogen gas. It reacts slowly with water producing a small amount of magnesium hydroxide. The reaction soon stops



as the magnesium hydroxide formed is almost insoluble and forms a barrier on the magnesium preventing further reaction.



Calcium, strontium and barium all react with cold water with increasing vigour to give the metal hydroxide and hydrogen gas. The hydroxides formed are not very soluble, but solubility increases down the group. Less precipitate is seen going down the group because more of the hydroxide dissolves in the water.

Reaction with acids

All the group II metals react with acids to produce salts and hydrogen gas. For example, magnesium reacts with hydrochloric acid to produce magnesium chloride and hydrogen gas.



The reactivity increases down the group. Calcium reacts vigorously with acids while barium reacts violently. When sulphuric acid reacts with barium, insoluble barium sulphate forms which coats the metal surface and prevents the inner barium from reacting.



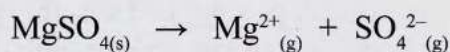
SOLUBILITY OF GROUP II COMPOUNDS

Solubility of solid compounds is determined by the energy required to break the lattice into ions (reverse of **lattice energy**) and the energy released when ions are hydrated (**hydration energy**). The energy required to break the lattice is endothermic while the hydration of the ions are exothermic. Low solubility results when the lattice energy exceeds the hydration energy.

The solubility of the sulphates

The solubility of the sulphates in group II decreases down the group. Dissolving a group II sulphate involves 3 main processes.

- Reverse of lattice energy ($-\Delta H_{\text{latt}}$)



- Enthalpy of hydration of the cation (ΔH_{hyd})



- Enthalpy of hydration of the anion (ΔH_{hyd})



Lattice energy is inversely proportional to the sum of the radius of the cation and the radius of the anion. From this, if either ionic radius increases, lattice energy decreases. The anion is constant since all the sulphates contain the SO_4^{2-} anion. The cation increases in size however this increase in size is negligible compared to the large size of the anion. Thus the increase in ionic radii is very small hence the decrease in lattice energy is very small.

As size of the cation increases down the group, the charge density decreases. This decreases the forces of attraction which develop with polar water molecules. Thus the hydration energy decreases.

Table 14.2a Some Enthalpies of Group II sulphates

	Lattice enthalpy	Hydration enthalpy of M^{2+}	Hydration enthalpy of SO_4^{2-}	Enthalpy of solution
MgSO_4	-2833	-1923	-1130	-220
CaSO_4	-2653	-1583	-1130	-60
SrSO_4	-2603	-1450	-1130	+23
BaSO_4	-2433	-1273	-1130	+30

Since the decrease in the reverse lattice energy is less when compared to the decrease in hydration energy, the enthalpy of solution for the sulphates become more positive going down the group. Therefore the solubility of the sulphates decreases down group II. If the dissolving process is exothermic, then the sulphate will be soluble, e.g. magnesium sulphate. However if the dissolving of the sulphate is endothermic, it will be sparingly soluble in water, e.g. calcium sulphate.

Table 14.2b Solubility of group II sulphates

Solubility in 100 g water	MgSO_4	CaSO_4	SrSO_4	BaSO_4
	600×10^{-4}	11×10^{-4}	0.6×10^{-4}	0.009×10^{-4}

Solubility of carbonates

Solubility of the carbonates decreases down the group. The decrease in solubility is similar to that of the sulphates. On going down the group, the decrease in lattice energy is small compared to the decrease in hydration energy. Thus the reverse lattice energy exceeds the hydration energy and the enthalpy of solution is positive.

Solubility of the hydroxides

The solubility of the hydroxides increases down the group. Since the hydroxide ion is not as large as the sulphate or carbonate ions, the lattice energy decreases significantly down the group. This

outweighs the change in the hydration energy so the solubility of the hydroxides of group II elements increases down the group.

Table 14.3 Variation in solubility

Sulphates and carbonates		Hydroxides	
Mg	↓ decrease in solubility	Mg	↓ increase in solubility
Ca		Ca	
Sr		Sr	
Ba		Ba	

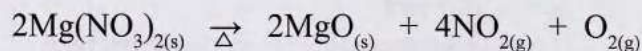


THERMAL STABILITY OF GROUP II COMPOUNDS

The compounds of group II elements have different thermal stabilities. This means that they decompose at different temperatures when heated. The thermal stability of a compound depends on the charges and the sizes of the ions in the compound.

Nitrates

The nitrates of group II undergo thermal decomposition to give the metal oxide, nitrogen dioxide and oxygen. For example

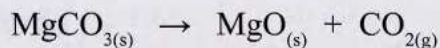


Going down the group, the nitrates become more stable so higher temperatures are required to decompose them. This means that the thermal stability of the nitrates of the group II elements increases down the group.

Decomposition of the nitrate involves breaking down the larger nitrate compound into a smaller more stable oxide compound. This is promoted by the polarizing effect of the cation that attracts the electron cloud of the nitrate ion. Smaller highly charged cations are more polarizing and tend to attract the electron cloud of the nitrate ion enough to weaken the structure and break the bonds. On going down the group, the cations get larger and the charge remains the same, so that there is less polarizing effect of the cation and the compound becomes more stable.

Carbonates

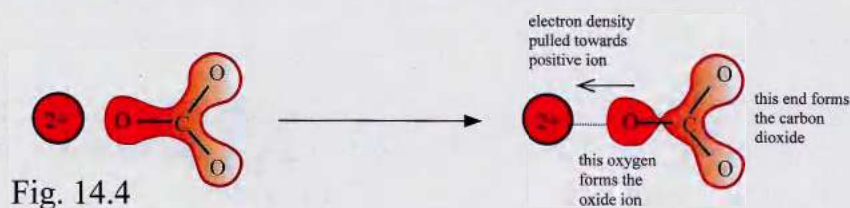
The carbonates of group II undergo thermal decomposition to give the metal oxide and carbon dioxide. For example



The small double positive charged ions at the top of the group polarize the carbonate ions more than the larger double positive



charged ions at the bottom. Thus the thermal stability of the carbonates of the group II elements increases down the group.



USES OF GROUP II ELEMENTS AND THEIR COMPOUNDS

Magnesium is the most commonly used element in group II. It is used to make lightweight alloys with high tensile strength. Magnalium is an alloy of Mg and Al. It is used in the manufacture of parts for cars and aircrafts. Magnesium oxide is used to make refractory lining in furnaces because of its high melting point and low reactivity. It is also used as a medication to relieve heartburn and acid indigestion since it is basic. In addition it can be used as a mild laxative. Magnesium sulphate on the other hand, is used as a powerful laxative. It is also used in beauty spas as a softening agent for the hands and feet.

Calcium, strontium and barium have less uses due to their high reactivity. Calcium compounds however do have significant commercial uses. Calcium carbonate is used in the construction industry as a building material, e.g. marble, or as an ingredient of cement. It is widely used in medicine as dietary calcium supplement and an antacid. Calcium carbonate, calcium oxide and calcium hydroxide are used in agriculture to counteract soil acidity. These are also used in water treatment to reduce acidity and as a flocculant. In the industry, they are used in scrubbers to desulphurize waste gases and to neutralize acidic effluents.

Calcium oxide also called quicklime reacts exothermically with water to form calcium hydroxide. The reaction produces sufficient heat to ignite combustible materials in some instances. In the 19th century, wooden boats were used to transport calcium oxide. The crew often had to extinguish fires when any of the calcium oxide reacted with water.

At high temperatures, salts of calcium, strontium and barium emit brilliant flame colours. Calcium salts produce a red colour while strontium salts produce a crimson colour and barium salts produce a green colour. Compounds of these elements are used in fireworks and coloured flares.



Questions

1. Explain the variation of the following in terms of structure and bonding of the elements in group II:
 - (a) atomic radii
 - (b) melting point
 - (c) 1st ionization energies
2. Describe the reactions of the group II elements with the following:
 - (a) oxygen
 - (b) water
 - (c) dilute hydrochloric acidUsing a named group II element, write equations for the reactions in (a) – (c) above.
3. With reference to the lattice energy and hydration energy, account for the variation of the solubility of the sulphates of group II elements.
4. Describe and explain how the thermal stability of the carbonates of the group II elements varies down the group. Write an equation for the decomposition of a carbonate of a named group II element.
5. Explain the variation in the thermal decomposition of the nitrates of the group II elements. Write an equation for the decomposition of a nitrate of a named group II element.
6. Account for the following as fully as you can:
 - (a) Magnesium sulphate is soluble in water while barium sulphate is not.
 - (b) Calcium carbonate decomposes at a lower temperature than barium carbonate.
 - (c) Magnesium reacts slowly with water whereas calcium reacts vigorously.



The group IV elements are carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). All have four electrons on the valence shell. There is a change in nature from non-metallic to metallic characteristics as we descend the group. Carbon is a non-metal, silicon and germanium are metalloids, and tin and lead are metals. Some of the physical properties of the elements as well as unique features of the elements are described below.



PHYSICAL PROPERTIES

The elements in group IV show characteristic trends in physical properties on descending the group. Table 15.1 below gives some properties of the group IV elements.

Table 15.1 Some properties of group IV elements

Element	Electronic configuration (outer shell only)	Atomic radius/nm	1 st ionization energy /kJ mol ⁻¹	Structure	Density/g cm ³	Melting point/°C	Conductivity
C	2s ² 2p ²	0.077	1090	Giant molecular	2.25 (diamond) 3.51 (graphite)	3730 Sublimes	Non-conductor Conductor
Si	3s ² 3p ²	0.117	786	Giant molecular	2.33	1410	Semi-conductor
Ge	4s ² 4p ²	0.122	762	Giant molecular	5.35	937	Semi-conductor
Sn	5s ² 5p ²	0.140	707	Giant metallic	7.28	232	Conductor
Pb	6s ² 6p ²	0.154	716	Giant metallic	11.30	327	Conductor

Atomic radius

Atomic radius increases as we descend group IV. This is expected as a full orbital is added from one successive element to the next down the group. The screening effect also increases as these full inner orbitals shield the outer electrons from the increasing nuclear charge. This results in the outer electrons being further from the nucleus causing an increase in the size of the atom. Although the proton number increases, the screening effect outweighs this



increase in nuclear charge.

Ionization energy

The ionization energy decreases down the group. Since the atomic radius increases down the group, the outer electrons get further away from the nucleus and less energy is required to remove an outer electron. There is a large difference in ionization energy from C to Si, after that the difference is relatively small as shown in Table 15.1. This is a consequence of the d-block elements within the periodic table. The d orbitals do not screen the nucleus as efficiently as the s and p orbitals thus the effective nuclear charge is higher. This results in little difference in the ionization energy after silicon.

Structure and bonding

The variation in the physical properties of the group IV elements is related to the change in structure of the elements from giant molecular to giant metallic. Silicon and germanium show a giant molecular structure similar to diamond while tin and lead have metallic structures. As the atom gets larger, the attraction of the nucleus for the electrons in the covalent bond gets weaker. This results in electrons becoming delocalized. The delocalized electrons are attracted to the positively charged nucleus hence bonding changes from covalent to metallic.

The change in bonding gives rise to the variation in the melting point and conductivity of the elements. Carbon exists mainly as graphite and diamond. In diamond, each carbon atom is covalently bonded to four other C atoms in a tetrahedral arrangement. Its melting point is 3730°C . No free electrons are present and hence it is a non conductor of electricity. In graphite, each carbon atom is bonded covalently to three other carbon atoms. The fourth electron of each carbon atom forms a delocalized electron cloud. This allows graphite to conduct electricity.

Silicon has a melting point of 1410°C and is referred to as a semi-conductor. Silicon forms a giant molecular structure having strong covalent bonds. Germanium has a melting point of 937°C and is also a semi-conductor. Tin has a melting point of 232°C and exists in the form of two allotropes, grey and white tin. Grey tin is a semi-conductor while white tin is a good conductor of electricity. Lead has a melting point of 237°C and is a good conductor of electricity.

The decrease in melting points reflects the increasing weakness of the covalent or metallic bonds as the atoms get bigger and the



bonds get longer.

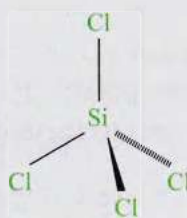
Bond	Bond energy/kJ mol ⁻¹	Bond length/nm
C-C	347	0.154
Si-Si	226	0.252
Sn-Sn	150	0.280

We know that the larger the bond energy, the stronger the bond. Also the shorter the bond length, the greater is the strength of the bond. Since C-C has the greatest bond energy and the shortest bond length, it has the strongest bond and has a high melting point.



THE TETRACHLORIDES OF GROUP IV

Carbon, silicon, germanium, tin and lead all form tetrachlorides with the formula XCl_4 . They are all simple covalent molecules with a tetrahedral shape. The group IV element is at the centre and bonds with four chlorine atoms by four single covalent bonds. The shape of the silicon tetrachloride is shown below.

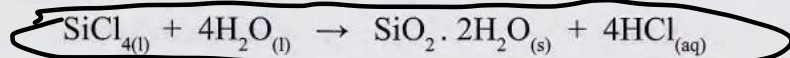


All the tetrachlorides have low melting and boiling points. They are volatile liquids at room temperature. As the X – Cl bond becomes longer down the group, it gets weaker and the tetrachlorides get less stable.



THE HYDROLYSIS OF THE TETRACHLORIDES OF GROUP IV

With the exception of tetrachloromethane, all of the tetrachlorides readily react with water to produce a precipitate of the hydrated dioxide and fumes of HCl. For example



Silicon, germanium, tin and lead all have empty d orbitals close enough in energy to the occupied p orbitals. These atoms allow incoming water molecules to donate a lone pair to their d orbitals to form a bond. For example in SiCl_4 , a water molecule can



donate a lone pair into the empty 3d orbitals of silicon to form a dative covalent bond. As the Si – O bonds form, the Si – Cl bonds weaken and break. The bonds make and break one by one until all four chlorine atoms are displaced. Thus hydrolysis of the tetrachloride occurs.

Tetrachloromethane (CCl_4) is immiscible in water and does not undergo hydrolysis. The empty 3d orbitals in carbon are too different in energy for carbon to expand its octet to form dative bonds with the water molecules. Thus a similar mechanism for hydrolysis cannot occur and tetrachloromethane shows no reaction in water.



THE OXIDES OF GROUP IV

Table 15.2 and table 15.3 below give some properties of the oxides of the group IV elements.

Table 15.2

Properties of the dioxides of group IV elements

The dioxides (+4 oxidation state)	Boiling point/ $^{\circ}\text{C}$	Structure	Acid-base nature	Thermal stability
CO_2	-78	Simple molecular	Acidic	Stable at high temperatures
SiO_2	2590	Giant molecular	Acidic	Stable at high temperatures
GeO_2	1200	Intermediate between giant molecular and ionic	Amphoteric	Stable at high temperatures
SnO_2	1900	Intermediate between giant molecular and ionic	Amphoteric	Stable at high temperatures
PbO_2	Decomposes on heating	Intermediate between giant molecular and ionic	Amphoteric	Decomposes on warming

Table 15.3

Properties of the monoxides of group IV elements

The monoxides (+2 oxidation state)	Structure	Acid-base nature	Thermal stability
CO	Simple molecular	Neutral	Readily oxidize to the dioxide
SiO	Simple molecular	Neutral	Readily oxidize to the dioxide
GeO	Predominantly ionic	Amphoteric	Readily oxidize to the dioxide
SnO	Predominantly ionic	Amphoteric	Readily oxidize to the dioxide
PbO	Predominantly ionic	Amphoteric	Stable



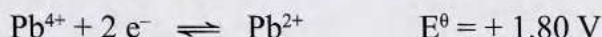
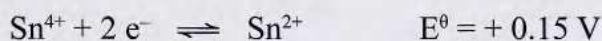
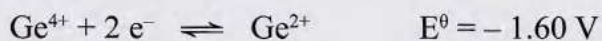
Bonding

All the elements in group IV have four electrons in their valence shell ($ns^2 np^2$). None form the X^{4+} ion in the solid state due to the high ionization energies required to remove four successive electrons from the atom. Consequently, bonding is covalent. Going down the group, germanium, tin and lead tend to form ionic compounds in which the group IV element has an oxidation state of +2. In these compounds, the Ge^{2+} , Sn^{2+} and Pb^{2+} ions are formed when the two p electrons are lost from the valence shell. The two s electrons remaining on the valence shell is relatively stable and not easily removed. This is because the effective nuclear attraction towards them is greater since the d orbitals do not screen the nucleus as efficiently as the s and p orbitals. This is called the **inert pair effect** and it occurs as a result of the two remaining electrons behaving inertly since the ionization energy required for their removal is very large.

Oxidation states

Compounds of group IV elements exist with oxidation states +2 and +4. The +4 state is most common in compounds. For example when the elements are heated in oxygen, with the exception of lead, they all form oxide with oxidation state +4. It must be noted however that the relative stabilities of the +2 state relative to the +4 state increase down the group as bonding changes from covalent to ionic. In carbon and silicon, the +4 state is more stable than the +2 state. CO is readily oxidized to CO_2 , while SiO is unstable and does not exist under normal conditions. Germanium, tin and lead tend to form ionic compounds and form oxides of both +2 and +4 state. GeO is less stable than GeO_2 , and is oxidized to GeO_2 . The +4 state in tin is slightly more stable than the +2 state while the +2 state in lead is more stable than the +4 state. The increase in stability of the +2 oxidation state on going down the group is explained in terms of the inert pair effect.

The standard electrode potentials of the $X^{4+}_{(aq)} / X^{2+}_{(aq)}$ for germanium, tin and lead can be used to show the relative stabilities of the +2 and +4 oxidation states of these elements.



As the standard electrode potentials get more positive from Ge^{4+} to Pb^{4+} , aqueous ions in the +4 state is more easily reduced to the

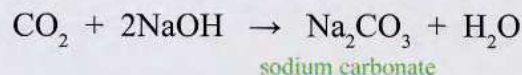
+2 state.

Acid-base nature of the oxides

The basic character of the oxides increases down the group. The dioxides are more acidic than the monoxides.

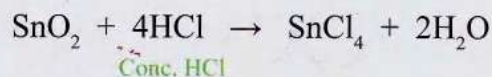
The dioxides

The bonding in CO_2 and SiO_2 is covalent. These oxides show acidic behaviour. They react with alkalis to form salts.

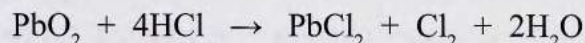


The bonding in GeO_2 , SnO_2 and PbO_2 shows both ionic and covalent character. These oxides are amphoteric. They show both acidic and basic properties.

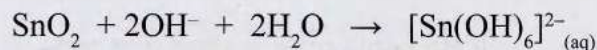
For example tin (IV) oxide reacts with concentrated hydrochloric acid to give SnCl_4 .



This dissolves in excess HCl to form the complex $[\text{SnCl}_6]^{2-}$. In the case of lead (IV) oxide, the reaction has to be done at low temperature because the lead (IV) chloride formed is unstable and decomposes to give lead (II) chloride and chlorine gas.



The dioxides also react with alkalis. For example, tin (IV) oxide reacts with concentrated sodium hydroxide solution to give the complex $[\text{Sn}(\text{OH})_6]^{2-}$.



In the case of lead (IV) oxide, molten sodium hydroxide is used.



The monoxides

CO and SiO are neutral and react neither with acids or alkalis. GeO , SnO and PbO are amphoteric. They all react with concentrated hydrochloric acid. For example, tin (II) oxide reacts with hydrochloric acid to form tin (II) chloride.



In the reaction with lead (II) oxide, insoluble lead (II) chloride is formed. This however dissolves in excess concentrated hydrochloric acid to form the soluble complex $[\text{PbCl}_4]^{2-}$.

GeO , SnO and PbO also react with bases. For example



SILICATES

Some geologists estimate that 90% of the Earth's crust is made up of silicates. The basic chemical unit of silicates is the SiO_4^{4-} tetrahedron. The central silicon ion has a charge of positive four while each oxygen atom has a charge of negative two. This condition leaves each oxygen atom with the option of bonding to another silicon ion and thus links one SiO_4^{4-} tetrahedron to another and another. Silicates tetrahedrons can combine to form chain, sheet and ring structures.



Fig. 15.1

In silicates, some of the negatively charged oxygen atoms are able to interact with positively charged ions like Mg^{2+} , Ca^{2+} and Al^{3+} . **Asbestos** is a single chain silicate which contains magnesium, calcium or iron ions. It is fire resistant and a poor conductor of heat. It is used as building material however care must be taken because exposure to asbestos fibers can cause lung cancer.

Talc is a sheet silicate containing magnesium ions. It is a soft, slippery material which is used in soaps and talcum powder. Clays are also sheet silicates but about half of the silicon atoms are replaced by aluminium atoms. They are also called aluminosilicates. When clay is wet, water is trapped between the sheets and the material becomes flexible and can be molded into different shapes. If the clay is heated at high temperatures, water is removed and a three dimensional giant structure similar to quartz is formed.

Ceramics is the name given to materials which are made from clay



and then heated at high temperatures. Ceramic products include pottery, bricks and tiles. More recently, ceramic production is geared towards crystalline ceramics which is considered to have superior properties to those that were produced in years before. These are designed to have properties such as hardness, strength and ability to withstand high temperatures for applications such as heat shields in spacecrafts, and armour protection in military vehicles.





Questions

1. Explain the variation of the following physical properties of the group IV elements in terms of structure and bonding.
 - (a) Melting point
 - (b) 1st ionization energy
 - (c) Metallic character
 - (d) Electrical conductivity
2. Group IV elements show the +2 and +4 oxidation states in many compounds.
 - (a) Account for the relative stability of the oxides of the group IV elements of oxidation states +2 and +4.
 - (b) What is the trend in the acid-base nature of the oxides of the group IV elements in the +4 oxidation state? Illustrate your answer with suitable equations.
 - (c) Describe the trend in bonding of the oxides of the group IV elements in the +4 oxidation state?
 - (d) Explain why carbon dioxide is a gas and silicon dioxide is a high melting point solid.
3. The group IV tetrachlorides are volatile, non-polar liquids.
 - (a) Draw the molecular shape of carbon tetrachloride.
 - (b) Explain why carbon tetrachloride is a non-polar molecule.
 - (c) Explain the trend in the volatility of the tetrachlorides of the group IV elements.
4. With the exception of tetrachloromethane, the tetrachlorides of group IV elements are readily hydrolysed by water.
 - (a) Write an equation for the hydrolysis of one of the tetrachlorides with water.
 - (b) Account for the unreactivity of tetrachloromethane with water.
5. Some properties of ceramics include hardness, strength and ability to withstand high temperatures. Explain the structure of silicon IV oxide which makes it suitable as the building block of ceramics.



The halogens are the elements found in group VII of the periodic table. They all contain seven electrons in their outermost shell and have the ability to accept an electron to gain an octet of electrons and hence take part in ionic bonding. The halogens also have the ability to share electrons in covalent bonding with itself as well as with other non metals in the periodic table. One of the most unique features of the halogens is its ability to exist as diatomic molecules when it combines with itself. The members of this group include fluorine, chlorine, bromine, iodine and astatine.

Since the element astatine has no stable or long-lived isotopes, most physical properties of astatine have been predicted from theory and by extrapolation from the properties of other elements.



VARIATION IN PROPERTIES

Properties of the halogens

Table 16.1

Property	Fluorine	Chlorine	Bromine	Iodine
Molecular formula	F ₂	Cl ₂	Br ₂	I ₂
Electron configuration of outer shell	2s ² 2p ⁵	3s ² 3p ⁵	4s ² 4p ⁵	5s ² 5p ⁵
Atomic radius/ nm	0.072	0.099	0.114	0.133
State at 20°C	gas	gas	liquid	solid
Colour	pale yellow	green	red-brown	purple
Melting point / °C	-220	-101	-7	114
Boiling point / °C	-188	-35	59	184
Bond energy / kJ mol ⁻¹	158	242	193	151
Standard electrode potential/ V	+2.87	+1.36	+1.09	+0.54
Electronegativity	4.00	2.85	2.75	2.20
Density (g/cm ³)	1.513	1.655	3.187	3.960

As we descend group VII, the number of electrons in the halogen increases as a fully filled energy shell is added. These added electrons give rise to an increase in atomic radius down the group. Also there is greater van der Waals forces of attraction since these electrons can move freely setting up temporary dipoles. These attractive forces which exist between the molecules increase as we descend the group.

These stronger intermolecular forces of attraction means that more energy is needed to break the bonds between the molecules. Therefore the melting point and boiling point increase as we descend the group. Thus the halogens become less volatile going down the group. The increase in the van der Waals forces of attraction also results in a change in the physical states of the molecules from a gas to a liquid to a solid. In addition, as the forces of attraction between the molecules increase, the molecules pack closer together thus the mass per unit volume increases i.e. the density increases.

The colour of the halogen molecules at room temperature gets darker as we descend group VII. The colour exhibited by these compounds is the complementary colour of the light they absorb from the visible region of the electromagnetic spectrum. Electrons absorb energy in the visible region of the spectrum and become promoted to a higher energy level. The colour of the molecules depends on the amount of energy the outer electrons absorb. Chlorine appears as a green gas, bromine is a dark red-brown liquid, iodine is a dark crumbly solid that sublimes into a purple vapour and astatine is a black solid.

As the atomic radius increases down the group, the bond length gets longer. It is expected that as the bond length increases, less energy would be required to break the $X - X$ bond. With the exception of fluorine, the bond energy of halogens decreases down the group. Since fluorine atoms are small, the lone pairs of electrons on the atom get close enough to set up a significant amount of repulsion within the molecule. This repulsion weakens the $F - F$ bond to give the unexpected low bond energy.



OXIDIZING AGENTS

An oxidizing agent is a species that has the ability to accept electrons. The halogens can all accept electrons as they all have at least one unpaired electron in their outer shell. However as we descend the group oxidizing ability decreases. This means that the ability of the halogens to accept electrons decreases down the group. The standard electrode potential values are a direct measure of the oxidizing ability of the halogens. The stronger oxidizing agent has more positive potential. Therefore standard electrode potentials can be used to predict the relative strengths of oxidizing agents.



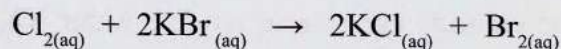
Table 16.2 Standard electrode potentials of the halogens

Reaction	E°/V
$F_2 + 2e^- \rightleftharpoons 2F^-$	2.87
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	1.36
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	1.09
$I_2 + 2e^- \rightleftharpoons 2I^-$	0.54

Fluorine is such a strong oxidizing agent that it oxidizes water to oxygen and so it is not possible to do simple aqueous reactions with it.



In the case of chlorine, bromine and iodine, a halogen higher in the group can oxidize the ions of one lower. For example, chlorine can oxidize the bromide ions to bromine and iodide ions to iodine.

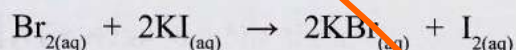


The bromine forms an orange solution.



The iodine dissolves in potassium iodide to give a red-brown solution.

Bromine can only oxidize iodide ions to iodine.

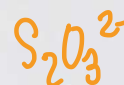


Iodine does not oxidize any of the halide ions above it.

Other oxidizing reactions

All halogens can oxidize sulphite ions to sulphate ions and hydrogen sulphide to sulphur. However, only fluorine, chlorine and bromine can oxidize iron (II) ions to iron (III) ions, and thiosulphate ions to sulphate ions. Iodine is too weak an oxidizing agent to oxidize iron (II) ions to iron (III) ions, and thiosulphate ions to sulphate ions. In the case of thiosulphate ions, it oxidizes the thiosulphate ions to tetrathionate ions.

Reaction of thiosulphate ions with iodine is



Reaction of thiosulphate ions with bromine is



Table 16.3 Oxidizing reactions of halogens

Oxidizing agent	Reaction
All halogens	Sulphite (SO_3^{2-}) $\rightarrow$ sulphate (SO_4^{2-})
All halogens	Hydrogen sulphide (H_2S) $\rightarrow$ sulphur (S)
Fluorine, chlorine, bromine	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$
Fluorine, chlorine, bromine	Thiosulphate ($\text{S}_2\text{O}_3^{2-}$) $\rightarrow$ sulphate (SO_4^{2-})
Iodine	Thiosulphate ($\text{S}_2\text{O}_3^{2-}$) $\rightarrow$ tetrathionate ($\text{S}_4\text{O}_6^{2-}$)

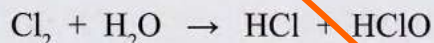


REACTION OF HALOGENS WITH WATER

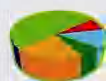
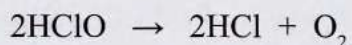
Fluorine and chlorine are able to oxidize water while bromine and iodine are not. Fluorine is such a strong oxidizing agent that it oxidizes water to oxygen.



Chlorine reacts slowly with water to form hydrochloric acid and chloric (I) acid (HClO).



Chloric (I) acid decomposes in sunlight to give oxygen.

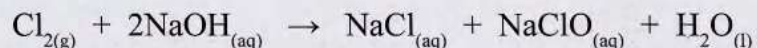


REACTION OF HALOGENS WITH ALKALI

Chlorine, bromine and iodine undergo similar reactions with alkalis. The products depend on the temperature at which the reaction is carried out.

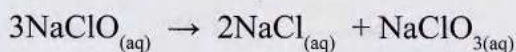
Cold dilute NaOH

When chlorine is added to dilute sodium hydroxide at about 15°C , a mixture of sodium chloride and sodium chlorate (I) is formed.



The sodium chlorate (I) produced in the reaction slowly decomposes to sodium chloride and sodium chlorate (V), NaClO_3 .

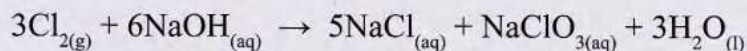




Both reactions are fast at 15°C for bromine and iodine. Decomposition of iodate (I) to iodate (V) occurs rapidly even at 0°C.

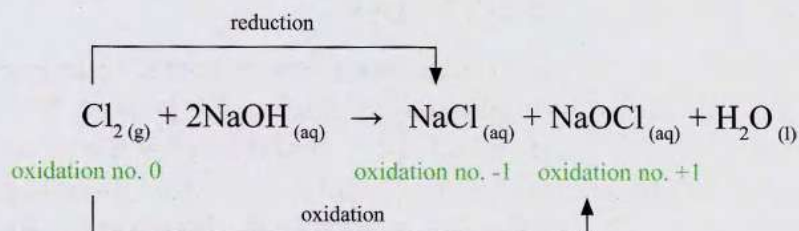
Hot dilute NaOH

When chlorine is bubbled directly into hot aqueous sodium hydroxide at about 70°C, a mixture of sodium chloride and sodium chlorate (V) is formed.



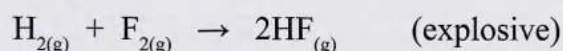
The reaction forms sodium chlorate (I) first which rapidly decomposes at 70°C to sodium chlorate (V). Sodium chlorate (I) is used as a mild antiseptic and is produced by bubbling chlorine into cold sodium hydroxide solution. Sodium chlorate (V) is used as a weed killer and is produced by bubbling chlorine into hot sodium hydroxide solution.

In the reactions of chlorine with sodium hydroxide, the chlorine molecule is simultaneously oxidized and reduced in each of the reaction. Reactions like these are called **disproportionation** reactions.

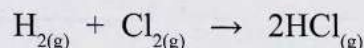


REACTIONS OF HALOGENS WITH HYDROGEN

The halogens react directly with hydrogen to produce hydrogen halides. The reaction between hydrogen and fluorine is explosive even at low temperatures.

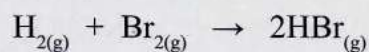


Hydrogen reacts with chlorine slowly in the dark and explosively in sunlight.

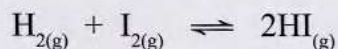


Bromine combines with hydrogen at high temperatures in the presence of a catalyst.





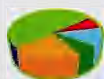
The reaction between hydrogen and iodine is slow and reversible giving a low yield.



The formation of hydrogen halides are likely to occur because they have negative enthalpy value, that is, the energy of the products is less than that of the reactants, making the products more stable. The enthalpy of a reaction is equal to the sum of the bond energy of the bonds broken minus the sum of the bond energy of the bonds formed. This is shown in table 16.4 below.

Halogen molecule	Bond energy \kJ mol ⁻¹	Hydrogen halide	Bond energy \kJ mol ⁻¹	$\Delta H^\circ/\text{kJ mol}^{-1}$
F ₂	158	HF	562	$(158 + 436) - (2 \times 562) = -530$
Cl ₂	244	HCl	431	$(244 + 436) - (2 \times 431) = -182$
Br ₂	193	HBr	366	$(193 + 436) - (2 \times 366) = -103$
I ₂	151	HI	299	$(151 + 436) - (2 \times 299) = -11$
H ₂	436			

Table 16.4



STABILITY OF HYDRIDES

The hydrogen halides are all colourless gases at room temperature and pressure except for hydrogen fluoride, which boils at 19°C due to strong hydrogen bonding. They dissolve in water to form strong acids. The strengths of the acids increase down the group i.e. HI > HBr > HCl > HF. This is because the bond energy for the hydrogen halides decreases down the group so they dissociate more easily. They dissociate according to the equation:



Table 16.5

Table showing bond lengths and bond enthalpies of Group VII Hydrides

Molecule	Bond length/nm	Bond Enthalpy/kJ mol ⁻¹
H-F	0.092	+562
H-Cl	0.128	+431
H-Br	0.141	+366
H-I	0.160	+299

From table 16.5, it can be seen that as we descend group VII, the bond lengths of the hydrides increase. Longer bonds are weaker

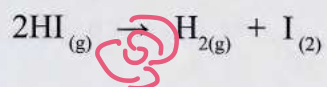
bonds. This implies that the stability of the group VII hydrides decreases as we descend group VII. This is also reflected by the decrease in bond enthalpies from HF to HI. Thus the stability of the hydrogen halides decreases as the group is descended.

how easily S
break down
when heated.

The thermal stability of the group VII hydrides can be experimentally verified by placing a hot nichrome wire into test tubes each containing HCl, HBr, and HI. No change is seen with the HCl. However, the HBr forms a reddish-brown gas since the hydrogen bromide dissociates to produce bromine gas.



In HI, a purple vapour of iodine is seen. Dissociation of HI takes place since the H – I bond is weak.



TESTS FOR HALIDE IONS

Most metal halides are soluble except silver and lead halide. Therefore solutions of lead and silver ions can be used to test for the presence of halide ions in solution. For example

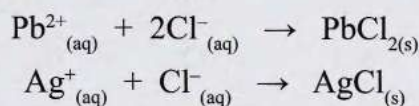


Table 16.6 The reactions of aqueous halide ions.

Reagent	$\text{F}^{-}_{(aq)}$	$\text{Cl}^{-}_{(aq)}$	$\text{Br}^{-}_{(aq)}$	$\text{I}^{-}_{(aq)}$
$\text{Pb}(\text{NO}_3)_2_{(aq)}$	White precipitate of PbF_2	White precipitate of PbCl_2	Cream precipitate of PbBr_2	Yellow precipitate of PbI_2
$\text{AgNO}_3_{(aq)}$	No reaction, AgF soluble in water	White precipitate of AgCl	Cream precipitate of AgBr	Yellow precipitate of AgI
Solubility of silver halide in (a) $\text{dil. HNO}_3_{(aq)}$ (b) $\text{dil. NH}_3_{(aq)}$ (c) conc. NH_3		insoluble soluble soluble	insoluble insoluble sparingly soluble soluble	insoluble insoluble insoluble
Effect of sunlight	No effect	White ppt. turns purple-grey	Cream ppt. turns green-yellow	No effect

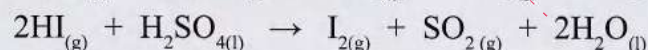
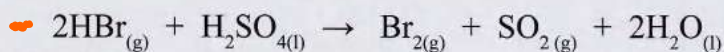
Solid halides react with concentrated sulphuric acid to form the hydrogen halides. When concentrated sulphuric acid is added to a solid halide, the first product is fumes of the hydrogen halide.



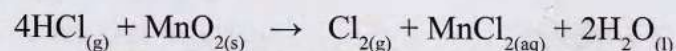
For example



Concentrated sulphuric acid is also an oxidizing agent and it is strong enough to oxidize HBr to Br_2 , and HI to I_2 . However it is not strong enough to oxidize HF and HCl.



When concentrated sulphuric acid is used in the presence of a stronger oxidizing agent such as MnO_2 , it can oxidize HCl to Cl_2 but HF is still not oxidized.



Concentrated sulphuric acid cannot be used for the preparation of $\text{HBr}_{(g)}$ and $\text{HI}_{(g)}$. Instead concentrated phosphoric (V) acid, H_3PO_4 , is used since it is a relatively poor oxidizing agent.



Table 16.7 The reactions of solid halides.

Reagent	Fluoride	Chloride	Bromide	Iodide
Conc. H_2SO_4	$\text{HF}_{(g)}$ formed	$\text{HCl}_{(g)}$ formed	$\text{HBr}_{(g)}$ and a little $\text{Br}_{2(g)}$ formed	$\text{HI}_{(g)}$ and $\text{I}_{2(g)}$ formed
Conc. $\text{H}_2\text{SO}_4 + \text{MnO}_2$	$\text{HF}_{(g)}$ formed	$\text{Cl}_{2(g)}$ formed	$\text{Br}_{2(g)}$ formed	$\text{I}_{2(g)}$ formed
Conc. H_3PO_4	$\text{HF}_{(g)}$ formed	$\text{HCl}_{(g)}$ formed	$\text{HBr}_{(g)}$ formed	$\text{HI}_{(g)}$ formed



Questions

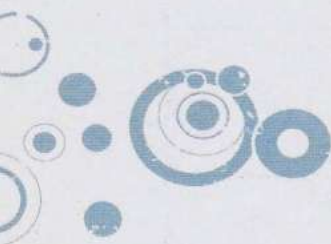
1. Explain the variation in the following physical properties of the elements in group VII in terms of structure and bonding:
 - (a) State
 - (b) Volatility
 - (c) Electronegativity
2.
 - (a) Describe the reactions of the halogens with hydrogen. Illustrate your answer with relevant equations.
 - (b) Describe how bond energies help to explain the trend in the relative stabilities of the hydrides of group VII elements.
3. The elements of group VII are all oxidizing agents, but some are more strongly oxidizing than others. With reference to the standard electrode potential values, explain the relative strength of chlorine, bromine and iodine as oxidizing agents. Illustrate your answer with relevant equations.
4.
 - (a) Describe the reactions of the halogens with the reducing agent sodium thiosulphate.
 - (b) Referring to the following standard electrode potential values:

Reaction	E°/V
$F_2 + 2e^- \rightleftharpoons 2F^-$	2.87
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	1.36
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	1.09
$I_2 + 2e^- \rightleftharpoons 2I^-$	0.54
$2SO_3^{2-} + 3H_2O + 4e^- \rightleftharpoons S_2O_3^{2-} + 6OH^-$	0.58
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	0.09

Explain the reactions of the halogens with thiosulphate ions.



5. Chlorine, bromine and iodine undergo similar reactions with alkalis. The products depend on the temperature at which the reaction is carried out. Describe the reactions that occur when chlorine is bubbled through
- (a) cold aqueous sodium hydroxide
 - (b) hot aqueous sodium hydroxide.
6. Account for the following observation as fully as you can:
- (a) When chlorine is bubbled through an aqueous solution of KI, the solution turns a red-brown colour.
 - (b) A yellow precipitate is formed when aqueous silver nitrate is added to a solution of KI.
 - (c) An orange vapour is seen when concentrated sulphuric acid is added to solid KBr.



The transition elements are in the d-block of the periodic table and form a transition between group II and group III of the periodic table. They are metals that form one or more stable ions with incompletely filled d orbitals. The transition metals have general similarities in their physical and chemical properties.

Fig. 17.1

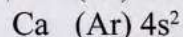
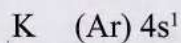
The Periodic Table

H																				e
Li	Be													B	C	N	O	F	Ne	
Na	Mg													Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		In	Sn	Sb	Te	I	Xe		
Cs	Ba		Hf	Ta	W	Rd	Os	Ir	Pt	Au	Hg		Tl	Pb	Bi	Po	At	Rn		
Fr	Ra																			

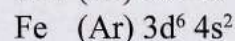
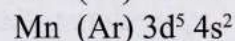
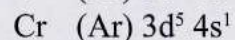
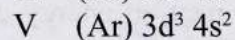
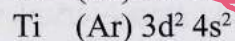
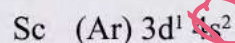
← transition metals →
d-block

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

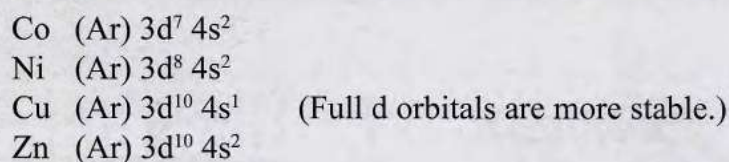
The d-block starts where the electrons start to fill the d orbitals. Remember, once the 3p orbitals are filled, the 4s orbital is filled before the 3d orbitals. Thus elements in the d block of the periodic table have their electrons with highest energy in a d orbital. Therefore in period 4, the electronic configurations of K and Ca are as follows:



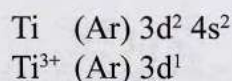
The d orbitals start to fill after calcium. The next ten elements are called the first row d block elements. Scandium is the first d-block element.



(Half-filled orbital are more stable)



It must be noted that when d-block elements form ions, it is the 4s electrons which are lost first. This occurs as a result of the 3d electrons repelling the 4s electrons further from the nucleus. Therefore, the 4s electrons are pushed to an energy level higher than 3d. Consequently, when a transition atom becomes an ion, the electrons from the 4s orbital are lost before those of the 3d. For example



Since a transition element is a d-block element that forms at least one stable ion with a partially filled d orbital, scandium and zinc are generally excluded as transition elements. Scandium only forms Sc^{3+} ions in its compounds and zinc only forms Zn^{2+} ions. The Sc^{3+} ion has no electrons in the d orbitals ($3d^0$) and the Zn^{2+} ion has completely filled d orbitals ($3d^{10}$). The chemistry of these metals shows only few of the characteristics associated with the transition metals.



PROPERTIES OF THE FIRST ROW TRANSITION ELEMENTS

The properties of the transition elements do not vary greatly across a period. Like other metals they are good conductors of heat and electricity, strong, hard, shiny, malleable and ductile. They differ from a typical s block metal such as calcium in the following ways:

- They have higher densities
- They have higher melting and boiling points
- They form coloured compounds and ions
- They form complex ions
- The compounds are often paramagnetic
- They often show catalytic activity
- They show variable oxidation states in their compounds

Moving left to right across the first row transition elements, properties such as atomic radius and ionization energy change relatively little across a transition series.



Table 17.1 Properties of 1st row transition metals

Element	Density/g cm ⁻³	Melting point / °C	Boiling point/ °C	Atomic radius/ nm	1 st ionization energy
Sc	2.99	1541	2831	0.164	631
Ti	4.50	1660	3287	0.147	658
V	5.96	1890	3380	0.135	650
Cr	7.20	1857	2670	0.129	653
Mn	7.20	1244	1962	0.137	717
Fe	7.86	1535	2750	0.126	759
Co	8.90	1495	2870	0.125	758
Ni	8.90	1455	2730	0.125	737
Cu	8.92	1083	2567	0.128	746
Zn	7.14	420	907	0.137	906

Atomic radius

The decrease in atomic radii from left to right across the first row of the d-block is small and irregular. The decrease is much less than that seen on moving across a short period such as sodium to argon. In the first row of the d-block, as the nuclear charge increases across the period, each additional electron enters the penultimate 3d orbital which increases the shielding experienced by the 4s electrons. This results in a relatively small difference in the effective nuclear charge as the shielding effect nullifies, to a large extent, the increase in nuclear charge. As the atomic radius decreases with increasing relative atomic mass, the density increases.

Ionization energy

The first ionization energy increases from left to right across the first row of the d-block. However the increase is relatively small compared to that of the short period sodium to argon. In the first row of the d-block, as the nuclear charge increases each additional electron enters the penultimate 3d orbital. These 3d electrons efficiently shields the 4s electrons from the nucleus. Thus the increase nuclear attraction for the outer 4s electrons is minimal across the period. This results in relatively small changes in the energy required to remove an outer 4s electron.

Melting and boiling points

The d-block elements form metallic structures. Electrons are available from both 4s and 3d orbitals for delocalization to form metallic bonds. This results in relatively high melting points and boiling points. The melting and boiling points drop at Mn and

Zn. This is because the extra stability of the half-filled Mn ($3d^5$) and filled Zn ($3d^{10}$) d orbitals make electrons less available to the cloud of electrons for metallic bonding. As a result the bonds are weaker and the melting and boiling points are lowered.



VARIABLE OXIDATION STATES

Calcium, for example, only has oxidation state number +2 in compounds due to ease at which 4s electrons are lost, but any further loss would need much greater energy since the third electron is to be found in an inner shell 3p orbital. Transition elements however form compounds with variable oxidation states due to the close similarity in energy of 4s and 3d electrons. The ionization energy increases only gradually as each successive electron is removed thus the electrons in both these orbitals can take part in bonding.

Table 17.2 Summarizes the known oxidation states for the first transition series.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
				+7					
			+6	+6	+6				
		+5	+5	+5	+5	+5			
	+4	+4	+4	+4	+4	+4	+4		
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
	+1	+1	+1	+1	+1	+1	+1	+1	

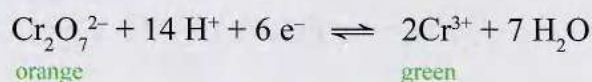
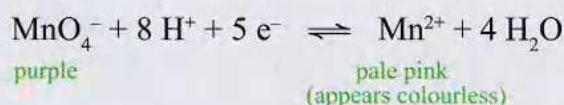
The oxidation states that are commonly encountered are in bold type, although they are not necessarily stable.

The following generalizations can be made from a study of the variable oxidation states of the transition metals:

- With the exception of Sc and Zn, all the elements show an oxidation state of +1 and +2 in their compounds. These correspond to bonding involving only the 4s electrons.
- The maximum oxidation number displayed by these elements implies that both the 4s and all of the unpaired 3d electrons are used in bonding. Mn can have an oxidation state of +7 since the maximum number of unpaired electrons available for bonding is 7. The number of unpaired electron decreases steadily on either side of Mn hence the pattern shown above.

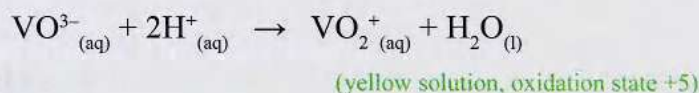
- Compounds containing transition metals in low oxidation states tend to be ionic in character (e.g. CuSO_4 , FeCl_2). Compounds in higher oxidation states tend to be bonded covalently to electronegative elements like oxygen or fluorine, forming polyatomic ions such as $\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^- .

Since oxidation numbers of the transition metals can vary in their compounds, they take part in many redox reactions. MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ are relatively strong oxidizing agents which show colour changes in redox reactions.

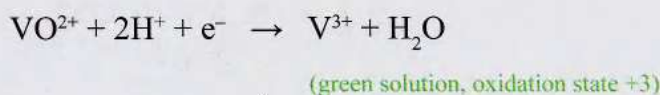


The chemistry of ammonium vanadate (V) in aqueous solution is a suitable example to show the variation in the oxidation states of vanadium. Vanadium has potentially 5 different oxidation states as its outer electronic configuration is $4s^2 3d^3$. Vanadium can be reduced from the +5 state right down to the +2 state by zinc. Each oxidation state of vanadium can be recognised by its colour.

Ammonium vanadate (V), NH_4VO_3 , is an orange solid. When about 2g of ammonium vanadate is added to 25 cm^3 of 2 mol dm^{-3} NaOH and then mixed with 50 cm^3 of 2 mol dm^{-3} H_2SO_4 , a yellow solution containing dioxovanadium (V) ions, VO_2^+ , is formed.



Shaking the dioxovanadium (V) solution with granulated zinc will cause a gradual transition of vanadium from the +5 to +2 oxidation state. The colour of the solution changes from yellow to green (mixture of VO_2^+ and VO^{2+}) then to blue (VO^{2+}) then to green (V^{3+}) and finally to violet (V^{2+}).

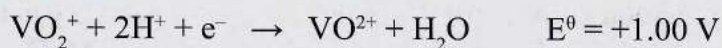




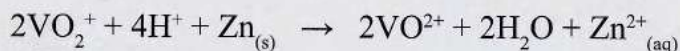
(violet solution, oxidation state +2)

Using E^{θ} values

When zinc is added to a solution of VO_2^{+} ions, the following half reactions are involved:



The overall cell reaction is

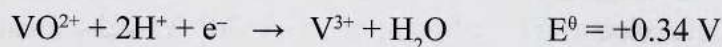


yellow

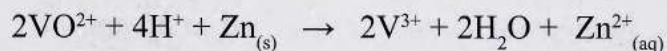
blue

$$\begin{aligned} E^{\theta}_{\text{cell}} &= 1.00 \text{ V} + 0.76 \text{ V} \\ &= +1.76 \text{ V} \end{aligned}$$

Once the VO^{2+} ions are formed it can then be reduced further to V^{3+} ions.



The overall cell reaction is



blue

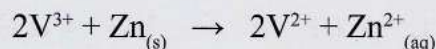
green

$$\begin{aligned} E^{\theta}_{\text{cell}} &= 0.34 \text{ V} + 0.76 \text{ V} \\ &= +1.10 \text{ V} \end{aligned}$$

Once the V^{3+} ions are formed it can yet be reduced further to V^{2+} ions.



The overall cell reaction is



green

violet

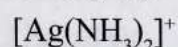
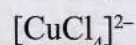
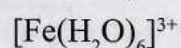
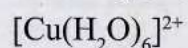
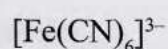
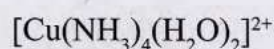
$$\begin{aligned} E^{\theta}_{\text{cell}} &= -0.26 \text{ V} + 0.76 \text{ V} \\ &= +0.50 \text{ V} \end{aligned}$$

Since the cell potential for each reaction is positive, zinc is able to gradually reduce vanadium from the +5 oxidation state to the +2 oxidation state.



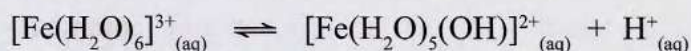
COMPLEX IONS

A complex ion consists of a central transition metal ion surrounded by other molecules or ions called **ligands**. A ligand is a neutral molecule or an anion with a lone pair of electrons which can be donated into the empty d orbitals of the central transition metal ion. Thus the ligands form co-ordinate bonds with the central ion. Some common ligands are H_2O , NH_3 , Cl^- and CN^- . Examples of complexes are:



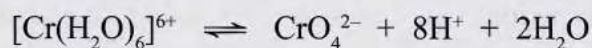
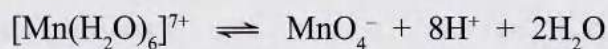
The number of co-ordinate bonds the ligand forms with the central ion is called the **co-ordination number** of the central ion. The most common co-ordination numbers are four and six however co-ordination number two is widespread in copper (I) and silver (I) compounds. In the examples above, the Cu^{2+} ion has a co-ordination number of six in $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, and four in $[\text{CuCl}_4]^{2-}$. The Fe^{3+} ion has a co-ordination number of 6 in $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$. Notice that the net charge on the complex ion is the resultant of the charge contributions from the central ion and the ligand.

When dissolved in water, transition metal ions form hydrated complexes with water molecules. The high charge density of the central ion polarizes the O – H bond of the water molecules causing the water molecules to become proton donors. Thus most aqueous solutions of transition metal compounds are acidic.



In compounds where the transition metal ion has an oxidation state higher than +3, the polarizing effect of the central ion is even greater in aqueous solution. This causes a loss of protons and water molecules resulting in the formation of the oxy-anions. For example, MnO_4^- and CrO_4^{2-} exist in aqueous solution instead of $[\text{Mn}(\text{H}_2\text{O})_6]^{7+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{6+}$ respectively.





Types of ligands

Ligands are classified according to the number of bonds they can form with the central ion. Some ligands have more than one site which can form a bond with the central ion. These are called **polydentate** ligands from the root words meaning “many tooth”. Note that the number of bonds formed is not equal to the number of lone pairs of electrons on the ligand. Each co-ordinating atom only donates one lone pair to the central ion.

Table 17.3 Types of ligands

Number of bonds formed by ligands	Ligand type	Example
1	Monodentate	H_2O , NH_3 , Cl^- , CN^-
2	Bidentate	$\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$
many	polydentate	EDTA

Ligands such as H_2O and NH_3 that share one lone pair with the central metal ion are known as monodentate or unidentate ligands. 1,2-diaminoethane (shortened ‘en’) is a bidentate ligand while the ethylenediaminetetraacetate ion (shortened EDTA) is a hexadentate ligand.

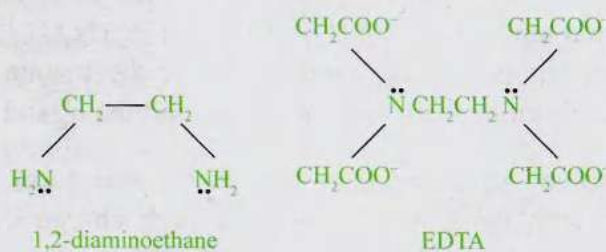
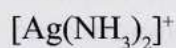
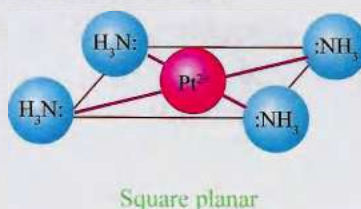
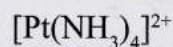
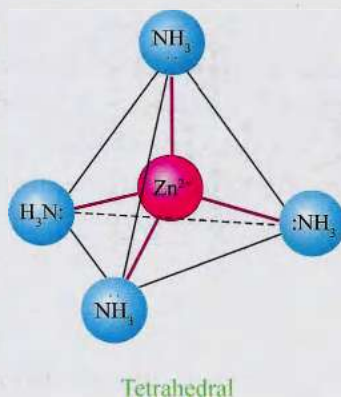
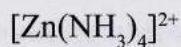


Fig 17.2

Shapes of complex ions

The shape of a complex ion depends on the number and type of ligands bonded to the central ion. In complexes with monodentate ligands, the central ions with co-ordination number 6 are octahedral in shape. Most complexes with co-ordination number 4 are tetrahedral while few show square planar shapes. Complexes with co-ordination number 2 give a linear shape.





Relatively few compounds adopt this shape, but these species are often useful, for examples, the anticancer drug Cisplatin ($\text{PtCl}_2(\text{NH}_3)_2$).

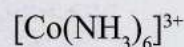


Fig 17.2

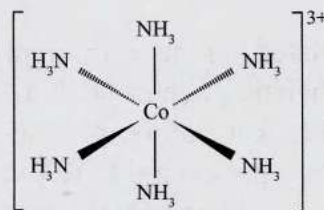
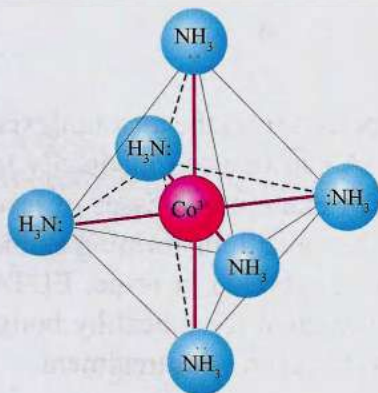


Fig 17.3 Shapes of complex ions

Ligands which bond to the metal ion with two or more pairs of electrons form ring complexes called **chelates**. The name comes from the Greek word meaning claw. In these complexes the ligands form a claw-like grip on the central ion. These complexes have enhanced stability as the central ion is held firmly by the ligands. The complex ion $[\text{Cr}(\text{en})_3]^{3+}$ contains three bidentate ligands co-ordinated around the chromium ion in an octahedral manner. Note that although there are only three ligands, the co-ordination number of the complex is still 6 as each ligand

forms two bonds to the central ion.

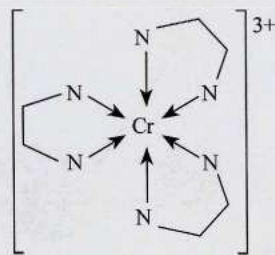


Fig 17.4



In $[\text{Zn}(\text{EDTA})]^{2-}$, the hexadentate ligand forms a very stable complex in which the metal ion is essentially wrapped up by the EDTA^{4-} ligand in an octahedral manner.

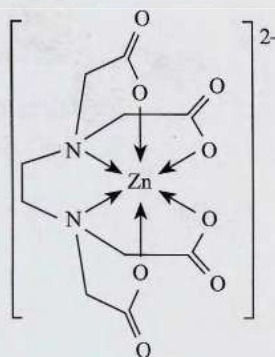


Fig 17.5



The chelated ions have different properties from the uncomplexed ions. Chelating agents such as EDTA can be used medically to treat d-block metal ion poisoning. For example, in cases of lead or mercury poisoning, EDTA traps the metal ions forming stable complexes. These complexes are then excreted in urine. EDTA also traps calcium ions which are important for a healthy body. Calcium supplements must therefore be taken with treatment.

Naming complex ions

The name of a complex ion has three parts.

- The first part indicates how many ligands are bonded to the central ion. The prefixes *mono*, *di*, *tri*, *tetra*, *penta* and *hexa* are used. Ligands that are anions, the name end in -o, e.g. F^- (fluoro), CN^- (cyano), Cl^- (chloro) and OH^- (hydroxo). Aqua is used for H_2O and ammine is used for NH_3 . When more than one type of ligand is present the names are written in alphabetical order.

- The second part indicates which metal it is. If the complex is positively charged, the English name is used. However, in negatively charged complexes, the Latin name with suffix *-ate* is used, e.g. aluminate, plumbate, cuprate, ferrate and zincate,
- The third part gives the oxidation state of the central metal. This is usually written in roman numerals and in brackets.

Examples

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is named hexaaquacopper (II) ion. Hexa means 6, aqua means the ligand is water, the metal is copper and the (II) tells us that the oxidation number of the copper is +2.

$[\text{CoCl}_2(\text{NH}_3)_4]^+$ is named dichlorotetraamminecobalt (III) ion. There are 2 chlorine ligands, 4 ammonia ligands and the metal is cobalt which has an oxidation number of +3.

$[\text{CuCl}_4]^{2-}$ tetrachlorocuprate (II) ion

$[\text{NiCl}_4]^{2-}$ is tetrachloronickelate (II) ion

$\text{Ni}(\text{CO})_4$ is tetracarbonylnickel (0)

$[\text{Ag}(\text{NH}_3)_2]^+$ is diamminesilver (I) ion

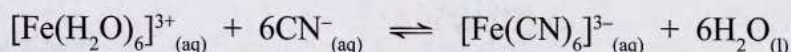
$[\text{Co}(\text{NH}_3)_6]^{3+}$ is hexaamminecobalt (III) ion

$[\text{Fe}(\text{CN})_6]^{4-}$ hexacyanoferrate (II) ion



LIGAND EXCHANGE REACTIONS

Some ligands form stronger bonds with a particular metal ion than other ligands. As a result stronger ligands may displace weaker ligands from a complex. For example, when cyanide ions are added to an aqueous solution of Fe^{3+} , the water ligands are replaced by the cyanide ligands.



Violet
(appears yellow in aqueous solution)

Prussian blue

This reaction is referred to as a **ligand exchange reaction**. The individual ligands are displaced stepwise, and an equilibrium expression could be written for each step, however it is more convenient to write an equilibrium expression for the overall ligand displacement reaction. This equilibrium constant is called the **stability constant**. Like all equilibrium constant, the stability constant varies with temperature.



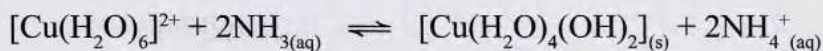
$$K_{\text{stab}} = \frac{[\text{Fe}(\text{CN})_6]^{3-}}{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}} [\text{CN}^-]^6$$

The stability constant measures the stability of the complex formed with respect to the aqua species. The values usually have a wide range and are often expressed as its logarithm, $\log K_{\text{stab}}$. The higher the value of the stability constant, the more stable is the complex formed. Thus the value of the stability constant gives an indication of tendency of a particular ligand to replace another ligand in a complex. Colour changes usually occur when the incoming ligands replace the existing ligands in a complex.

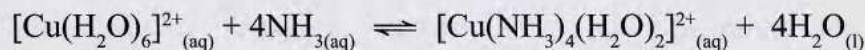
Table 17.4 The stability constants of some complexes

complex	K_{stab}	$\lg K_{\text{stab}}$
$[\text{Fe}(\text{CN})_6]^{4-}$	1×10^{24}	24
$[\text{Fe}(\text{CN})_6]^{3-}$	1×10^{31}	31
$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	1.2×10^{13}	13.1
$[\text{CuCl}_4]^{2-}$	4.2×10^5	5.6
$[\text{Cu}(\text{EDTA})]^{2-}$	6×10^{18}	18.8
$[\text{Co}(\text{NH}_3)_6]^{2+}$	8×10^4	4.9
$[\text{Co}(\text{NH}_3)_6]^{3+}$	5×10^{33}	33.7
$[\text{Co}(\text{EDTA})]^{2-}$	2×10^{16}	16.3
$[\text{Co}(\text{EDTA})]^-$	1×10^{36}	36

Ligand exchange reactions can be interpreted in terms of stability constants. For example, copper (II) sulphate forms the blue hexaaquacopper (II) ions, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ in solution. On adding aqueous ammonia, a pale blue precipitate is formed which is soluble in excess ammonia to give a deep blue solution. The ammonia acts as both a base and a ligand. With a small amount of ammonia, the ammonia ions accept hydrogen ions from the water ligands attached to the copper (II) ion to form a pale blue precipitate of copper (II) hydroxide.



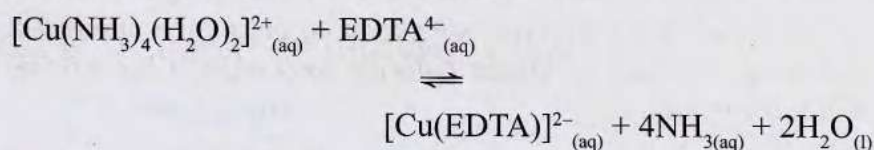
This precipitate is often written as $\text{Cu}(\text{OH})_2$, without including the water ligands. In excess of ammonia, the water ligands are replaced to form tetraamminediaquacopper (II) ions.



The position of equilibrium for the reaction of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions with excess ammonia lies to the right. Therefore as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

ions are used up in the reaction, the $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2]$ precipitate dissolves to restore $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions.

If EDTA is added to the deep blue solution $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ ions, the colour lightens as the ammonia and water ligands are replaced by the hexadentate EDTA ligands.

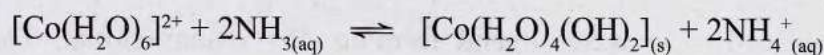


If concentrated hydrochloric acid is added to a blue solution of copper (II) sulphate, the solution turns green and then yellow. The chloride ions gradually replace the water ligands in the blue $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions to form a yellow solution of $[\text{CuCl}_4]^{2-}$ ions. The equilibrium mixture of the blue $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions and the yellow $[\text{CuCl}_4]^{2-}$ ions give the green colour. Dilution of the solution reverses the colour change.

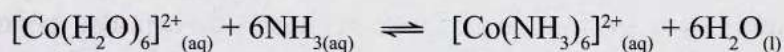


Adding water to the system has the effect of moving the position of equilibrium to the left. Thus the water molecules replace the chloride ions and the solution returns to blue.

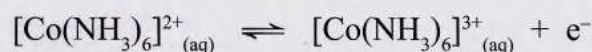
In the case of cobalt complexes, cobalt (II) chloride forms the pink hexaaquacobalt (II) ions, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, in solution. On adding aqueous ammonia, a green precipitate is formed which is soluble in excess ammonia to give a light brown solution. The light brown solution is oxidized in air or with an oxidizing agent such as hydrogen peroxide to form the dark brown cobalt (III) complex.



In excess of ammonia, the water ligands are replaced to form hexaamminecobalt (II) ions.



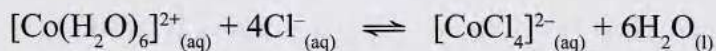
The hexaamminecobalt (II) ions are oxidized to hexaamminecobalt (III) ions.



If concentrated hydrochloric acid is added to a pink solution of cobalt (II) chloride, the solution turns blue. The high concentration of chloride ions shifts the equilibrium to the right. This causes the



chloride ions to replace the water ligands in the pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions to form a blue solution of $[\text{CoCl}_4]^{2-}$ ions.



Adding water to the system shifts the position of equilibrium to the left. Thus the water molecules replace the chloride ions and the solution returns to pink. Notice the co-ordination number of the cobalt changes as bigger chloride ions replace the smaller water molecules.

Haemoglobin

Haemoglobin is found in red blood cells. It consists of four globular proteins. At the centre of each protein is a Fe^{2+} ion complex known as haem. The Fe^{2+} ion has a co-ordination number 6. Five of the co-ordination sites are occupied by nitrogen, four from a planar ring structure called a porphyrin and the fifth from one of the protein. Water or a molecular oxygen ligand can reversibly attach itself to the sixth site.

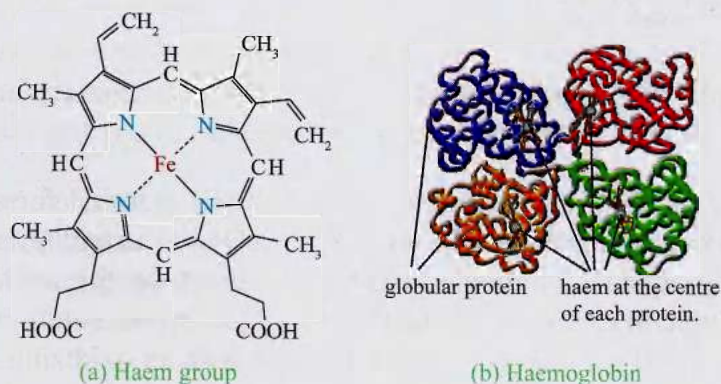


Fig. 17.6

In the lungs, oxygen attaches to the Fe^{2+} ion forming oxyhaemoglobin. In the other parts of the body, the oxygen is replaced by a water ligand forming deoxyhaemoglobin. This allows haemoglobin to transport oxygen in the blood from the lungs to the other parts of the body. Haemoglobin is capable of transporting 4 molecules of oxygen at any one time. Stronger ligands such as cyanide and carbon monoxide can also bond to this site. However, they bond irreversibly to the site and prevent haemoglobin from transporting oxygen in the body. This accounts for the poisonous nature of these substances.

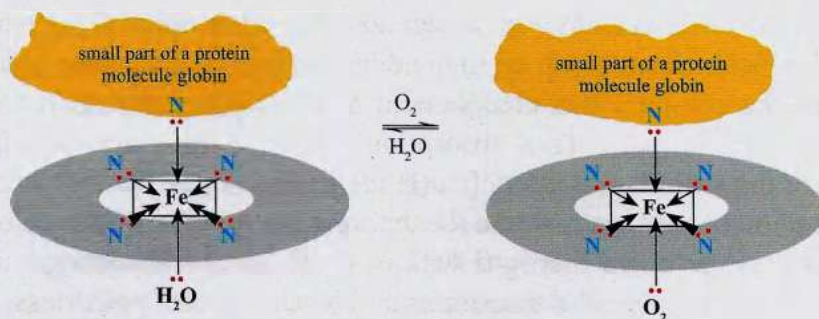


Fig. 17.7

Water and oxygen ligands can be reversibly bonded to the Fe^{2+} complex.



COLOURED COMPOUNDS

Transition metal ions show a wide range of colours, both in the solid state and in solution. Most of them form coloured complexes when surrounded by co-ordinating ligands. For example, anhydrous copper (II) sulphate is white but in aqueous solution it is blue. This is a result of the interaction between the water ligands and the d orbitals of the Cu^{2+} ion. In the isolated Cu^{2+} ion, the five d orbitals are degenerate (of the same energy). However, when the Cu^{2+} ion is surrounded by water ligands, the 3d orbitals closer to the ligands are pushed to a slightly higher energy level than those orbitals that are further away. This causes the five 3d orbitals to split into two groups of different energies. In tetrahedral complexes, three of the d orbitals experience more repulsion and are pushed to a higher energy level. In octahedral complexes, two of the d orbitals experience more repulsion and are pushed to a higher energy level. The splitting of the d orbitals in tetrahedral and octahedral complexes is shown below in Fig. 17.8.

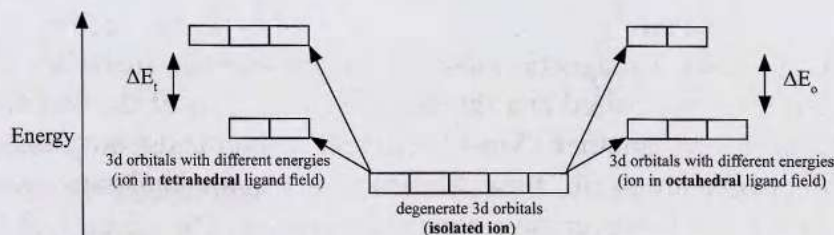


Fig. 17.8 Splitting of d orbitals

The magnitude of the energy ΔE depends on the strength of the electrostatic field caused by the lone pairs of the ligand. Thus different ligands give rise to different ΔE values.

A substance appears coloured if it absorbs light in the visible region of the electromagnetic spectrum. The energy gap ΔE between the split orbitals for most transition metal complexes corresponds to energies in the visible region of the spectrum. Therefore electrons

in the lower d energy level can absorb visible light of particular frequencies and jump up to the d higher energy level. The colour of the complex is a complement of the colours absorbed from the visible light. Thus absorption of visible light is responsible for the colours observed. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ absorbs in the red/orange region of the spectrum and the the solution appears blue in colour. It must be noted that ions with d^0 or d^{10} electronic arrangement have no possible d-d transitions and hence appears colourless. So ions like Ti^{4+} and Sc^{3+} (both $3d^0$), and Cu^+ and Zn^{2+} (both $3d^{10}$) generally do not give rise to coloured compounds.

Table 17.5 Some coloured ions

Ions	colour
$\text{Cr}_2\text{O}_7^{2-}(\text{aq})$	orange
$[\text{Cu}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$	blue
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$	pale green
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$	yellow/brown
$\text{MnO}_4^-(\text{aq})$	purple
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$	green
$[\text{Ni}(\text{NH}_3)_6]^{2+}(\text{aq})$	lilac/blue
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$	purple



MAGNETISM

Materials may be classified by their response to externally applied magnetic fields as diamagnetic, paramagnetic or non-magnetic.

Diamagnetic materials are repelled from the magnetic field, **paramagnetic** materials are attracted to the magnetic field and non-magnetic materials are not affected by the magnetic field.

All atoms have sources of magnetism because the electron spin contributes a magnetic moment. In diamagnetic materials, the electrons are paired and the magnetic moments of the electrons cancel one another. Most chemical compounds are weakly diamagnetic as all their electrons are paired. Paramagnetic substances however have unpaired electrons. The strength of the paramagnetism depends on the the number of unpaired electrons present.

Table 17.6 Magnetic moments

Unpaired electrons	Magnetic moment
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92



Many transition metal complexes are paramagnetic because they contain unpaired d electrons. The number of unpaired electrons in the non degenerate d orbital is related to the energy gap ΔE in the complex. If ΔE is small, the electrons occupy both high and low energy orbitals to avoid inter-electron repulsion. This is described as a '**high spin**' complex. If ΔE is large, the electrons occupy only the lower orbitals since it is more energetically worthwhile. This is described as a '**low spin**' complex. Fig. 17.9 below shows how Fe^{2+} ion can show diamagnetic or paramagnetic properties depending on whether the complex is high spin or low spin.

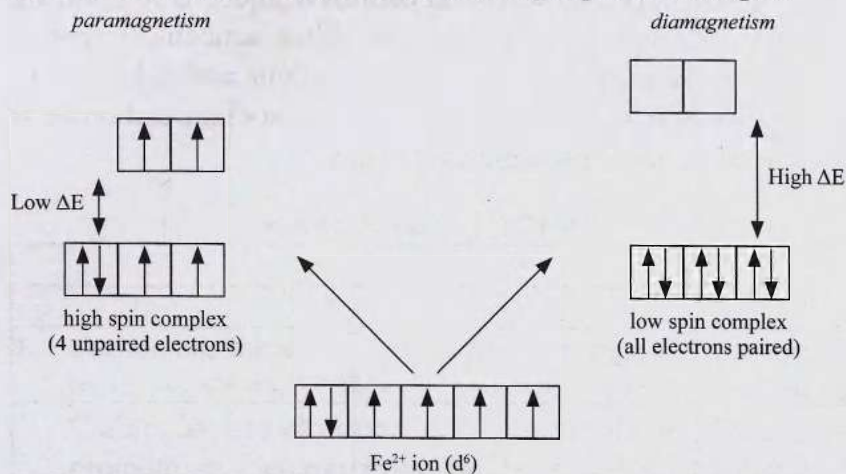


Table 17.9 Magnetic properties of Fe^{2+}

Iron, nickel and cobalt exhibit a unique magnetic behaviour which is called **ferromagnetism**. Ferromagnetic materials tend to stay magnetized to some extent after being subjected to an external magnetic field.



TRANSITION METALS AS CATALYSTS

Many transition metals and their compounds show catalytic properties because of their ability to change oxidation state and in the case of the metals, to adsorb other substances on to their surface. They provide an alternative pathway which has lower activation energy than that of the uncatalyzed reaction. All of this is discussed in the kinetics section.

Catalysts are very important in the chemical industry. For example, iron is used as a catalyst in the Haber process, and vanadium (V) oxide is used in the Contact process. Humans and many other living organisms require some transition metals to be present as trace elements in their diet, as they are essential for the many catalytic activities of enzymes. For example, the enzyme cytochrome oxidase, which is involved in the metabolism of food, requires copper.





INORGANIC QUALITATIVE ANALYSIS

Qualitative analysis of a substance involves adding a reagent to the unknown substance to convert it into a new compound which has characteristic properties such as its colour and solubility. Reagents should be added gradually until no further change is observed and gases evolved should be tested.

Test for cations

The usual reagents used to test for cations in aqueous solution are dilute aqueous sodium hydroxide and dilute aqueous ammonia. Cations can be identified based on the colour and solubility of the hydroxide formed. Sometimes aqueous sodium carbonate is added to precipitate insoluble carbonates.

Table 17.7 Tests for cations

	Reaction with	
	NaOH (aq)	NH ₃ (aq)
Al ³⁺ (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
NH ₄ ⁺ (aq)	no ppt., ammonia gas produced on heating	
Ba ²⁺ (aq)	no ppt.	no ppt.
Ca ²⁺ (aq)	white ppt. insoluble in excess	no ppt.
Cr ³⁺ (aq)	grey-green ppt. soluble in excess to give a dark green solution	grey-green ppt. insoluble in excess
Cu ²⁺ (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess to give a deep blue solution
Fe ²⁺ (aq)	green ppt. insoluble in excess	green ppt. insoluble in excess
Fe ³⁺ (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
Mg ²⁺ (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
Mn ²⁺ (aq)	off-white ppt. insoluble in excess	off-white ppt. insoluble in excess
Pb ²⁺ (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
Zn ²⁺ (aq)	white ppt. soluble in excess	white ppt. soluble in excess

Pb²⁺ ions can be distinguished from Al³⁺ ions by the insolubility of the lead (II) halides.



Test for gases

Reactions which liberate gases require that the gases be tested. In these cases, the gases are tested while they are generated in the reaction. When a gas needs to be tested in an aqueous solution such as calcium hydroxide, the gas is bubbled into the solution. When the gas is tested with materials such as moist litmus paper and a lighted splint, the material is placed at the mouth of the test tube where the gas is escaping.

Table 17.8 Test for gases

Gas	Test & Results
ammonia NH_3	turns moist red litmus paper blue
carbon dioxide CO_2	forms a white ppt. with Ca(OH)_2 solution
chlorine Cl_2	bleaches moist litmus paper
hydrogen H_2	lighted splint goes out with a 'pop'
hydrogen chloride HCl	forms dense white fumes with ammonia gas
nitrogen dioxide NO_2	a reddish-brown gas which turns moist blue litmus paper red
oxygen O_2	relights a glowing splint
sulphur dioxide SO_2	turns $\text{K}_2\text{Cr}_2\text{O}_7$ (aq) from orange to green

Flame tests

Flame tests are used to test solid compounds for cations. It involves dipping the tip of a metal wire such as platinum or nichrome into a little hydrochloric acid to clean it. Then the wire is dipped into the powdered sample and placed in the flame of a Bunsen burner. The cations present in the compounds give characteristic colours.

Table. 17.9
Flame tests

Cation	Colour
K^+	Lilac
Na^+	Bright yellow
Ca^{2+}	Brick-red
Ba^{2+}	Pale green
Cu^{2+} (halide)	Blue-green
Cu^{2+} (non halide)	Green
Sr^{2+}	Crimson





Fig. 17.10

Flame test on copper sulphate Flame test on sodium carbonate

Tests for anions

Reaction with dilute acid

CO_2 gas liberated indicates the presence of CO_3^{2-} ions

SO_2 gas liberated indicates the presence of SO_3^{2-} ions

Reaction with $\text{Ba}^{2+}(\text{aq}) / \text{H}^+(\text{aq})$

Yellow ppt., insoluble in dilute acid indicates the presence of CrO_4^{2-} ions

White ppt., insoluble in dilute acid indicates the presence of SO_4^{2-} ions

White ppt., soluble in dilute acid and CO_2 liberated indicates the presence of CO_3^{2-} ions

White ppt., soluble in dilute acid and SO_2 liberated indicates the presence of SO_3^{2-} ions

Reaction with $\text{Ag}^+(\text{aq}) / \text{H}^+(\text{aq}) / \text{NH}_3(\text{aq})$

Red-brown ppt., soluble in $\text{NH}_3(\text{aq})$ indicates the presence of CrO_4^{2-} ions

White ppt., soluble in $\text{NH}_3(\text{aq})$ indicates the presence of Cl^- ions

Cream ppt., partially soluble in $\text{NH}_3(\text{aq})$ indicates the presence of Br^- ions

Yellow ppt. insoluble in $\text{NH}_3(\text{aq})$ indicates the presence of I^- ions

Reaction with iron (II) sulphate followed by conc. H_2SO_4

A brown ring formed at the junction of the two liquids indicates the presence of NO_3^- ions

Reaction with Al powder followed by NaOH

NH_3 gas evolved indicates the presence of NO_3^- ions

Reaction with conc. HNO_3 followed by ammonium molybdate

A yellow ppt. indicates the presence of PO_4^{3-} ions.

Reaction with Fe^{3+} (aq)

A blood red colour indicates the presence of SCN^- ions

Reaction with alkaline Fe^{2+} (aq) / H^+ (aq) / Fe^{3+} (aq)

A blue ppt. indicates the presence of CN^- ions

Reaction with Pb^{2+} (aq) / H^+ (aq)

White ppt., insoluble in dilute acid and unaffected by heat indicates the presence of SO_4^{2-}

White ppt., soluble in dilute acid and CO_2 liberated indicates the presence of CO_3^{2-} ions

White ppt., soluble in dilute acid and SO_2 liberated indicates the presence of SO_3^{2-} ions

White ppt., insoluble in dilute acid and dissolves on heating and re-precipitates on cooling indicates the presence of Cl^- ions or Br^- ions

Yellow ppt. insoluble in dilute acid indicates the presence of I^- ions or CrO_4^{2-} ions

Reaction with Na_2CO_3 (aq)

No ppt., CO_2 gas liberated indicates the presence of an acid or an acid salt

White ppt., CO_2 gas liberated indicates the presence of Al^{3+} ions

Red-brown ppt., CO_2 gas liberated indicates the presence of Fe^{3+} ions

White ppt. indicates the presence of Ca^{2+} , Mg^{2+} , Pb^{2+} , Zn^{2+} or Ba^{2+} ions

White ppt., rapidly turning brown indicates the presence of Mn^{2+} ions

White ppt., darkening on heating indicates the presence of Ag^+ ions

Green ppt. indicates the presence of Fe^{2+} or Cr^{3+} ions

Blue ppt. indicates the presence of Cu^{2+} ions





Questions

- List four characteristic properties of transition metals.
 - Account for the relatively small changes in atomic radii and 1st ionization energies of the first row transition metals.
 - With reference to atomic size and structure explain why transition metals have higher melting points and higher densities than s block metals.
- Write the electronic configuration of the following:
 - Cu
 - V
 - Zn
 - Fe²⁺
 - Ni²⁺
- Define the term *ligand*.
 - Account for the formation of coloured ions by transition metals.
 - Explain why zinc is not considered a transition metal.
- Account for the following observation in terms of formation of complexes:
 - Anhydrous copper (II) sulphate forms the blue solution in water. On adding aqueous ammonia, a pale blue precipitate is formed which is soluble in excess ammonia to give a deep blue solution. If EDTA is added to the deep blue solution, the colour lightens.
 - If concentrated hydrochloric acid is added to a blue solution of copper (II) sulphate, the solution turns green and then yellow. Dilution of the solution reverses the colour change.
 - Cobalt (II) chloride forms the pink solution in water. On adding aqueous ammonia, a green precipitate is formed which is soluble in excess ammonia to give a light brown solution. The light brown solution turns dark brown on standing.
 - If concentrated hydrochloric acid is added to a pink solution of cobalt (II) chloride, the solution turns blue. Dilution of the solution reverses the colour change.



5. (a) Transition metals can exist in variable oxidation states. Suggest an explanation for this.
(b) Shaking an acidified solution of ammonia vanadate (V) with granulated zinc causes a gradual change in colour of the solution from yellow to green to blue then to green again and finally to violet. Explain this observation as fully as you can.
6. Explain why Cr^{6+} ions do not exist but CrO_4^{2-} ions are formed instead.
7. Iron is an important component of haemoglobin in blood.
(a) Describe the function of haemoglobin in the body.
(b) The presence of carbon monoxide in the body can inhibit the function of haemoglobin. Use the ligand exchange theory to explain how this can occur.
8. (a) Part of the Periodic Table is shown below.

					N			Ne
Na				Al			S	Cl
	Ca	Fe						
							I	
	Ba			Pb				

Write an ion of an element shown in the table above which gives the following reactions:

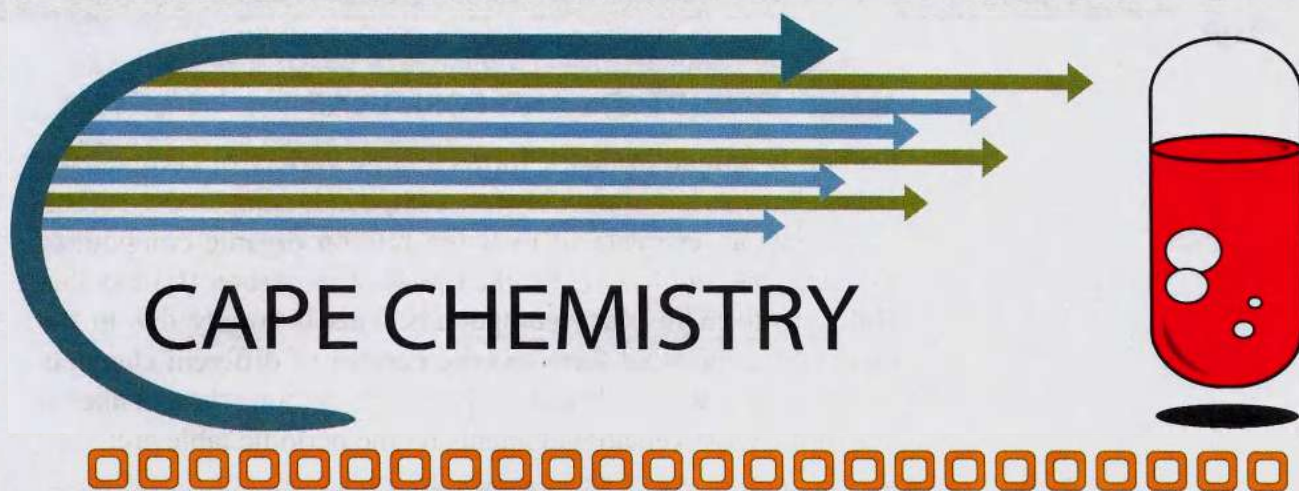
- (i) Forms a yellow precipitate with acidified aqueous silver nitrate.
 - (ii) Forms a white precipitate with aqueous lead (II) nitrate.
 - (iii) Burns with a bright yellow flame.
 - (iv) Forms no precipitate with aqueous sodium hydroxide.
9. Y is a powdered mixture containing a soluble and an insoluble salt. Water is added to sample Y and the mixture is filtered. The residue and filtrate are treated as follows:
 - (a) The residue dissolves in dilute nitric acid and liberates a colourless gas which forms a white precipitate with aqueous calcium hydroxide. The resulting solution reacted with both aqueous ammonia and sodium hydroxide to form an insoluble green precipitate.



- (b) The filtrate reacted with acidified barium chloride to form a white precipitate. It also reacted with aqueous ammonia and sodium hydroxide to form an insoluble white precipitate.

Using the given data above, deduce the possible ions present in the residue and the filtrate.





SECTION 4

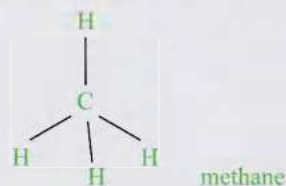
Chemistry of Carbon Compounds



STRUCTURE AND FORMULAE

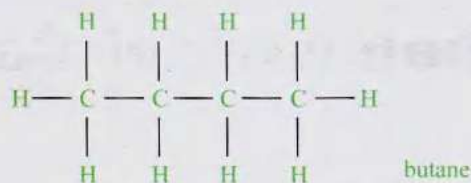
Carbon is unique in that it forms a large variety of compounds. Other elements have relatively few compounds compared to carbon which has an estimate of over ten million organic compounds to date. One would wonder then as to why carbon (C) has this ability to form so many compounds. This is largely due to the types of bonds it can form and the number of different elements that can bond with it. Some properties of carbon which makes it one of the most versatile elements on the periodic table are:

- Carbon is tetravalent which means it has four electrons on its outermost shell that are available for covalent bonding. For example, in methane the tetravalent carbon atom can form a covalent bond with each of four hydrogen atoms.

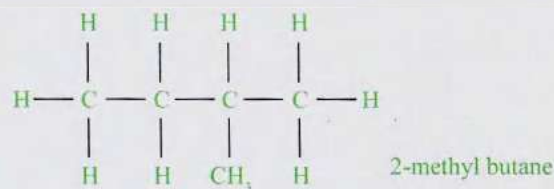


- Carbon has the ability to bond with other carbon atoms to form straight chains, branched chains and ring compounds with interconnecting C-C bonds. This property is called **catenation**. Carbon-carbon bonds are fairly strong, and abnormally stable. This property is important as it allows carbon to form a large number of compounds.

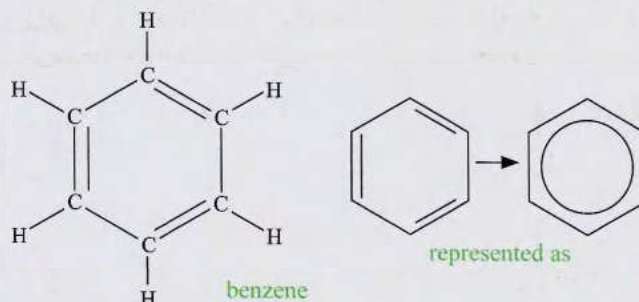
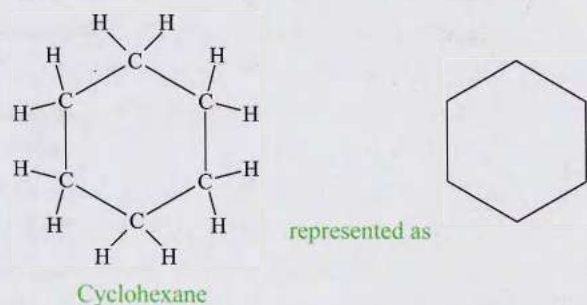
Straight Chain e.g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$



Branched Chain e.g. $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$



Ring Structures



- Carbon has the ability to mix and rearrange the four orbitals in the outer shell. This property is called **hybridization**. Carbon has the electronic configuration $1s^2 2s^2 2p^2$ and can promote an electron from the 2s orbital to the empty 2p orbital. Since both the 2s and the 2p subshells are half-filled, the excited state is relatively stable.

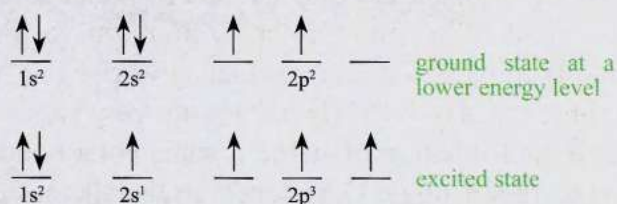


Fig. 18.1 Stable half-filled orbitals in the excited state

Two or more atomic orbitals can mix to create new orbitals of equal energy called hybrid orbitals. If the s orbital and all three p orbitals mix, then four hybrid orbitals of equal energy level are formed. This type of mixing is called sp^3 hybridization.

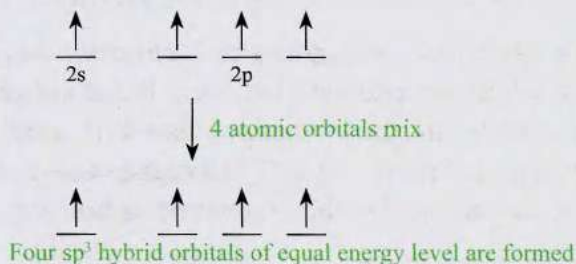


Fig. 18.2 sp^3 hybridization

Similarly, if the s orbital and two of the p orbitals mix, then,



three sp^2 hybrid orbitals of equal energy level are formed.

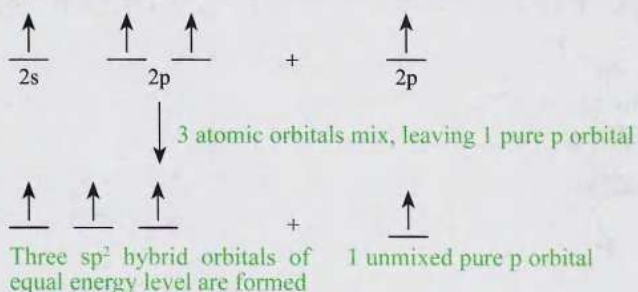


Fig. 18.3 sp^2 hybridization

Also when the s orbital and one of the p orbitals mix, two sp hybrid orbitals of equal energy level are formed.

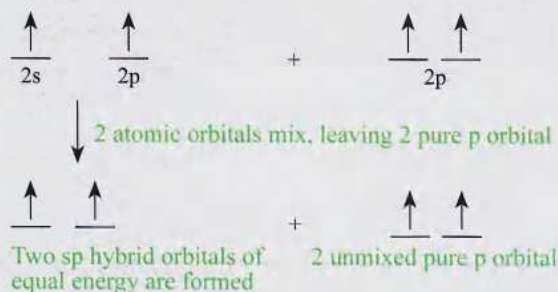


Fig. 18.4 sp hybridization

As a result of hybridization, carbon can form single, double and triple bonds with itself. The four sp^3 hybrid orbitals allow carbon to form four single bonds. In sp^2 hybridization, one of the sp^2 hybrid orbitals and the one pure p orbital give rise to a double bond. While in sp hybridization, one of the sp hybrid orbitals and the two pure p orbitals give rise to a triple bond. All three types of bonding pattern are very strong and contribute to the formation of stable organic compounds. In the alkanes there are single C–C bonds, in the alkenes there are C=C double bonds and in the alkynes there are C≡C triple bonds.

Homologous series

Organic compounds can be placed into various well-defined groups called homologous series e.g. alkanes, alkenes and alcohols. The members of a homologous series conform to the following:

- They all have the same **general formula**, that is, a common relationship exists between the numbers of different atoms in these compounds. For example, ethene (C_2H_4) and propene (C_3H_6) have the same general formula C_nH_{2n} where n is the number of carbon atoms in the compound.
- Each member differs from its nearest neighbour by a

molecular mass of 14 or a CH_2 group. For example, the molecular mass of ethene (C_2H_4) is 28 whereas that of propene (C_3H_6) is 42, a mass difference of 14 or a CH_2 unit.

- They all have the same functional group. For example, all alkenes have a double bond ($\text{C}=\text{C}$) whereas all the alcohols have a hydroxyl (OH) group.
- They have similar chemical properties because reactivity is determined by the functional group and since they have the same functional group they will react similarly.
- Physical properties vary directly to the number of C atoms in the homologous series.

Empirical formula

This is the simplest whole number ratio showing the atoms that combine to form a compound. For example, CH_2 is the empirical formula of all alkenes.

To calculate the empirical formula from the percentage mass of a compound:

- Divide the percentage of each element by its atomic mass to convert to moles.
- Divide the values obtained by the smallest number to find the ratio of moles.
- If need be multiply by a common factor to bring all to whole numbers.

Example 1

When butene was analyzed it was found to contain 85.72% carbon and 14.28% hydrogen. To calculate its empirical formula, the following steps are done:

Element	C	H
Percentage	85.72 %	14.28 %
Divide by atomic mass	$85.72 / 12 = 7.14$	$14.28 / 1 = 14.28$
Divide by smaller ratio	$7.14 / 7.14 = 1$	$14.28 / 7.14 = 2$
Empirical formula is CH_2 .		

Molecular formula

The molecular formula shows the actual number of each kind of atom in a molecule. It is a simple multiple of the empirical formula. For example the empirical formula of butene is CH_2 whereas the molecular formula is C_4H_8 .

To calculate the molecular formula of a compound, the empirical formula mass and the molar mass of the compound are required.



Since the molecular formula is a multiple of the empirical formula, then

$$n \times \text{the empirical formula mass} = \text{molar mass}$$

where n is a multiple.

Therefore

$$n = \text{molar mass} / \text{the empirical formula mass}$$

Once n is determined, we can multiply the subscript of each atom in the empirical formula by n to get the molecular formula.

Example 2

Quantitative elemental analysis shows that the empirical formula of a compound is CH. The molar mass is found to be 78g. What is the molecular formula?

Empirical formula mass of CH is $(12\text{g} + 1\text{g}) = 13\text{g}$
Using the formula

$$n \times \text{empirical formula mass} = \text{molar mass}$$

$$n \times 13\text{g} = 78\text{g}$$

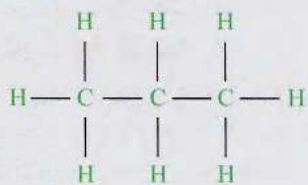
$$n = 78\text{g} / 13\text{g}$$
$$= 6$$

$$\therefore \text{Molecular formula} = 6 \times (\text{CH}) = \text{C}_6\text{H}_6.$$

Structural formula

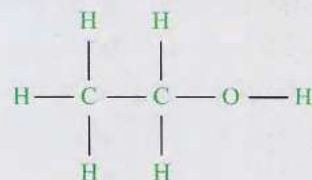
The structural formula shows the bonds in the molecule. It can be expressed as:

- **displayed formula** where all the bonds are clearly shown with the location of the atoms. For example



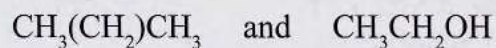
propane

and



ethanol

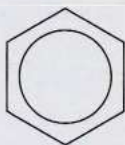
- **Condensed structural formula** which shows the placement of atoms in the molecule. For example



Propane

ethanol

Benzene (C_6H_6) is represented as



NAMING OF ORGANIC COMPOUNDS

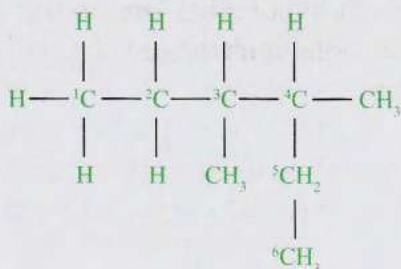
IUPAC nomenclature

The International Union of Pure and Applied Chemistry is the governing body in the world that is responsible for naming organic compounds. They have developed several rules which are used to allocate names for the millions of organic compounds that exist today.

Naming alkanes

Alkanes are described as *aliphatic* or *alicyclic* compounds. Aliphatic compounds are those organic compounds with straight or branched chains while alicyclic compounds contain rings of carbon atoms. When naming an organic compound the following rules apply:

- Look for the longest unbranched chain in the molecule.



Longest unbranched chain is 6 C atoms.

- Look for the branches / side groups attached to the main chain and locate which C atoms they are attached to.

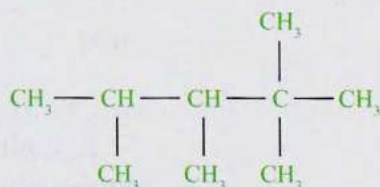
On the 3rd carbon there is a methyl group

On the 4th carbon there is another methyl group

- The name will be 3,4 – dimethyl hexane. In this example numbers are separated from each other by commas and numbers are separated from names by a dash.



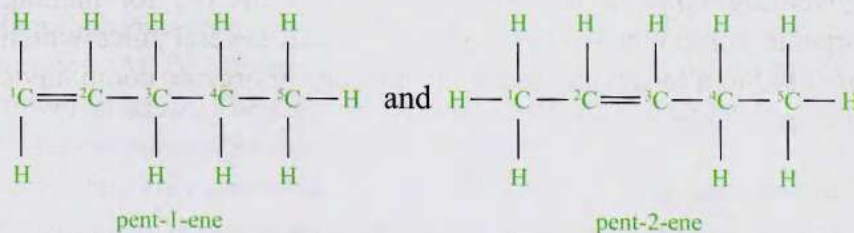
Consider the structure below



The name will be the longest unbranched chain prefixed by the name of the side groups and the number of the carbon atoms to which they are attached to.

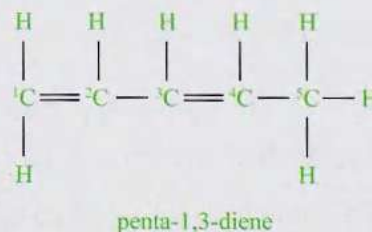
Naming alkenes

Alkenes with four or more carbon atoms can display structural isomerism. For example



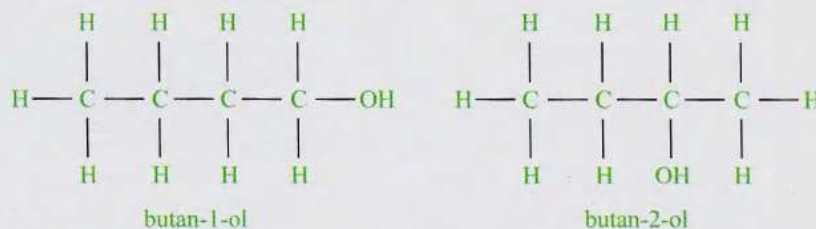
The position of the first unsaturated carbon must be given in the name, that is to say the position of the double bond must be specified. Pent-1-ene has a double bond between the first and second carbon atom while pent-2-ene has a double bond between the second and third carbon atom.

If the molecule has more than one double bond, then the position of each double bond must be given also the prefix takes an extra 'a'. For example,

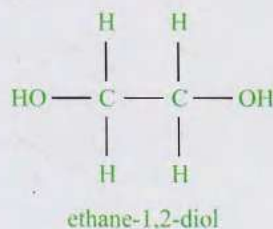


Naming alcohols

Like alkenes, the position of the hydroxyl must be given in the name. The alcohols also exhibit structural isomerism and so the position of the functional group is important in identifying the different isomers that can exist.



When more than one hydroxyl groups are present, the position must be stated. For example,



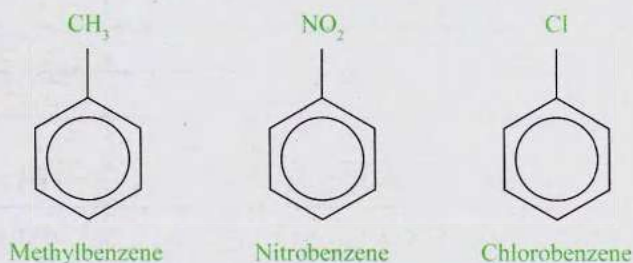
Here one of the two hydroxyl groups is attached to the first carbon atom and the other is attached to the second carbon atom.

Naming phenols

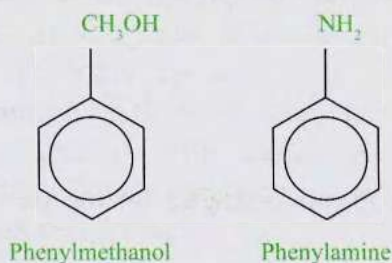
In phenol, the hydroxyl (OH) group is attached directly to the benzene ring and the compounds are named as in the naming of aromatic compounds

Naming aromatic compounds

Aromatic compounds also known as **arenes** are derived from benzene. Aromatic compounds can be named by identifying the groups attached to the benzene ring. For example



The carbon atom bearing the substituent group is assigned the number one carbon atom, so it is no surprise that some books quote the name of compounds with the numerical value one in front of the name, e.g. nitrobenzene is also written as 1-nitrobenzene. Aryl groups are derived from benzene or from a benzene derivative by removing a hydrogen atom that is bonded to the benzene ring. The radical from benzene is called "phenyl" and is used to identify the C_6H_5 group. For example,



Molecules with two substituent groups can show structural isomerism. For example,

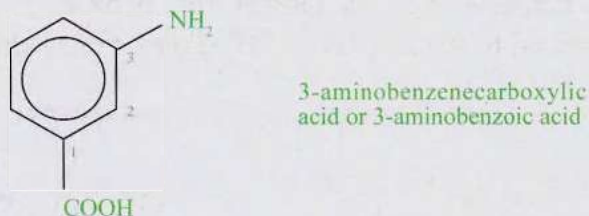


Groups in the 2 and 6 positions are said to be in the “ortho” positions while groups in the 3 and 5 positions are said to be in the “meta” positions. The 4th carbon atom is the “para” position. Table 18.1 below gives the IUPAC names of some derivatives of benzene:

Table 18.1
Names and
formulae of
some benzene
derivatives.

Structural formula	IUPAC Name	Traditional name
$C_6H_5NH_3Cl$	Phenylammonium chloride	Anilinium chloride
C_6H_5COOH	Benzenecarboxylic acid	Benzoic acid
$C_6H_5CO_2C_2H_5$	Ethyl benzenecarboxylate	Ethyl benzoate
C_6H_5COCl	Benzenecarbonyl chloride	Benzoyl chloride
$C_6H_5CONH_2$	Benzenecarboxamide	Benzamide
C_6H_5CN	Benzenecarbonitrile	benzonitrile
C_6H_5CHO	Benzenecarbaldehyde	benzaldehyde
$C_6H_5COCH_3$	Phenylethanone	
C_6H_5OH	Phenol	
$C_6H_5NH_2$	Phenylamine	Aniline
$C_6H_5OCH_3$	Methoxybenzene	

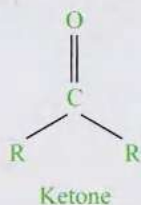
The list is placed in order of priority such that when there are two or more substituent groups on the ring, the group which is nearest to the top of the list is given the number one position on the benzene ring. For example,



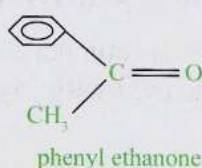
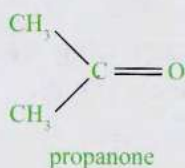
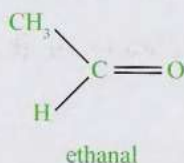
The $-COOH$ group is higher on the list and is given position one.

Naming aldehydes and ketones

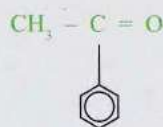
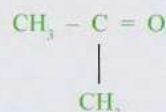
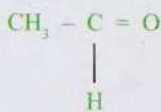
Compounds that have the carbon-oxygen double bond ($\text{C}=\text{O}$) or the carbonyl group are called carbonyl compounds. Aldehydes and ketones are carbonyl compounds. Aldehydes have at least one hydrogen atom attached to the carbonyl carbon atom while ketones have two R-groups (aliphatic or aromatic) attached.



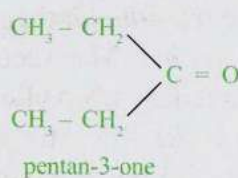
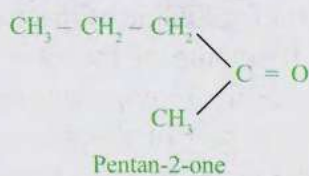
They are named as a derivative of the parent alkane. The 'e' in the alkane is changed to 'al' for the aldehydes while 'one' is added for the ketone.



These can also respectively be drawn as follows:

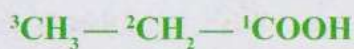


If the ketone shows structural isomerism, the position of the carbonyl carbon must be stated.



Naming carboxylic acids

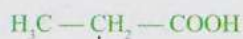
Aliphatic carboxylic acids are also named as a derivative of its parent alkane. The ending 'ane' is replaced by 'anoic acid'. The carbon atom in the COOH is always given the number one position.



propanoic acid



hexane-dioic acid or
hexane-1,6-diacid



2-phenyl propanoic acid



When naming aromatic carboxylic acid, the name carboxylic acid is added to benzene. For example,



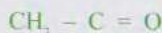
Benzenecarboxylic acid



Benzene 1,4-dicarboxylic acid

Naming of acid derivatives

Acyl halides are named by replacing the 'oic' ending of the carboxylic acid with 'oyl'. For example,



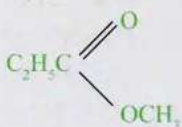
ethanoyl chloride



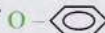
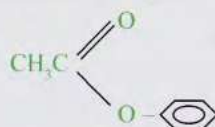
benzoyl iodide or
benzenecarbonyl iodide

Naming esters

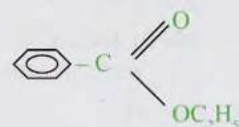
Esters are named as the aliphatic or aromatic salt of the parent carboxylic acid. The first part of the name of the ester is derived from the alkyl portion of the alcohol. This means that if the ester is made from *methanol* then the first part of the name of the ester would be *methyl*. The second part of the name of the ester is derived from the carboxylic acid. For example, if *propanoic acid* is used to make the ester then the second part of the name of the ester would be *propanoate*. Thus the name of ester formed from methanol and propanoic acid would be *methyl propanoate*. However it must be noted that the acid part is written first in the molecular and structural formula.



methyl propanoate



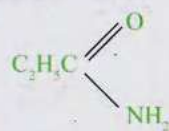
phenyl ethanoate



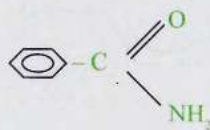
ethyl benzenecarboxylate
or ethyl benzoate

Amides

In amides, the 'oic acid' is replaced by the 'amide'.



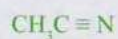
Propanamide



benzenecarboxamide or benzamide

Nitriles

Nitriles contain the cyano group ($\text{C} \equiv \text{N}$) on the carbon skeleton. If no other functional group is attached to the carbon chain, then the 'oic acid' is replaced by 'onitrile'.

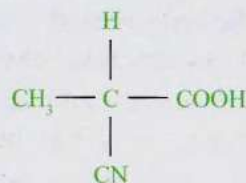


Ethanonitrile



benzenecarbonitrile or benzonitrile

If another functional group is attached to the carbon chain, it takes the prefix 'cyano'.



2- cyano propanoic acid.

Amines

Amines are derivatives of ammonia. They are classified as primary, secondary and tertiary amine depending on the number of R (alkyl or phenyl) groups attached to the nitrogen atom. They are named by adding the 'alkyl' or 'phenyl' prefix to 'amine'. When one R group is attached to the nitrogen atom, a primary amine is formed. If two R groups are attached to the nitrogen atom then a secondary amine is formed. Three R groups attached to the nitrogen atom give rise to a tertiary amine.



ethyl amine
(1° amine)

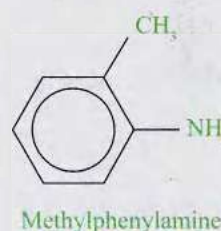


diethyl amine
(2° amine)



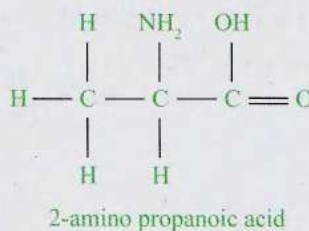
methyl diethyl amine
(3° amine)

If the amine shows structural isomerism, the position of the R group is stated. For example,



“N” is used to show the methyl group is attached to the nitrogen.

When amines contain other functional groups, the name ‘amino’ is used. For example,



ISOMERISM

Isomerism occurs when an organic molecule has the same molecular formula but different structural formula. Isomers are classified into two main groups as shown below.

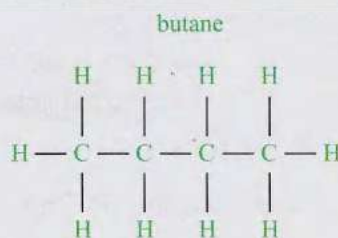
- **Structural isomers** – this is where atoms are linked together in different bonding orders.
- **Stereoisomers** – this is where atoms are attached in the same bonding order but are placed differently in space.

Structural isomers

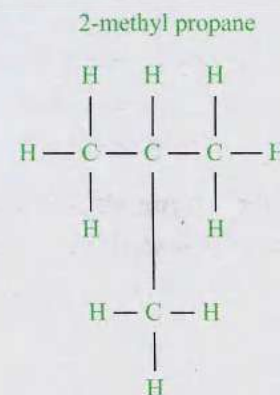
There are three main types of structural isomers.

- **Chain isomers** - these have different arrangement of carbon chains, but belong to the same homologous series. For example,

alkanes

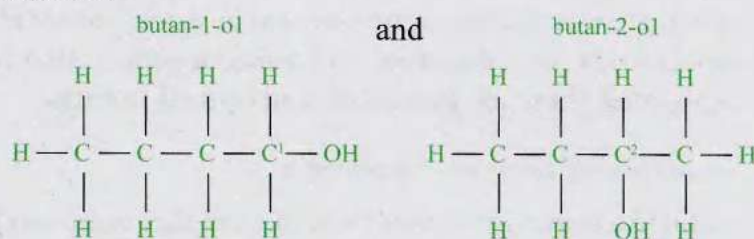


and

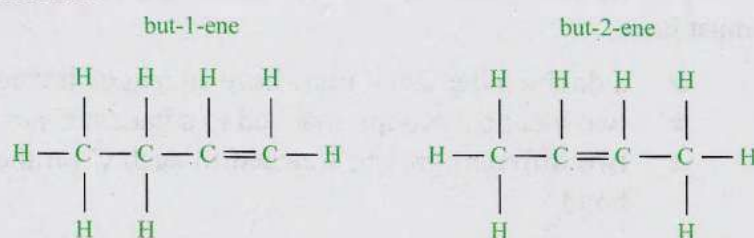


- **Positional isomers** - these have functional groups located at different positions on the same carbon skeleton. They have the same functional groups and belong to the same homologous series. For example,

alcohols

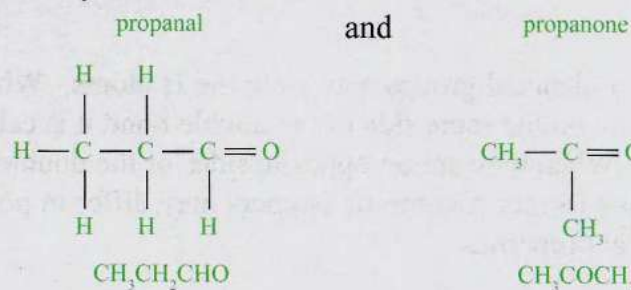


alkenes

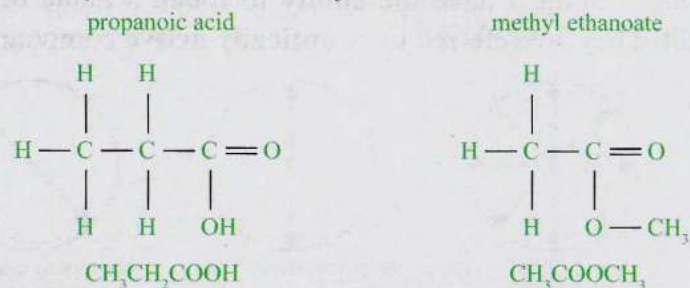


- **Functional group isomers** - these exist between compounds which have different functional groups and belong to different homologous series. For example,

an aldehyde and a ketone



a carboxylic acid and one of its ester



Stereoisomerism

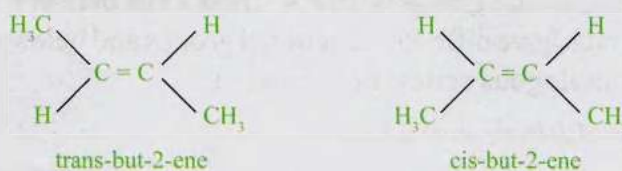
Stereoisomers are compounds which have the same molecular and structural formula but different spatial arrangements of atoms or groups of atoms. These isomers are different from each other only in the way the atoms are oriented in space, but are alike with respect to the way the atoms are linked together. Two types are highlighted, these are **geometric** and **optical** isomers.

Geometric or cis-trans isomerism

Geometric isomerism arises from the fact that compounds which contain double bonds show restriction of rotation about the $C = C$. Organic compounds which exhibit geometric isomerism must have

- a double bond i.e. it must have an alkene linkage.
- two identical groups attached to adjacent C atoms.
- two different groups attached to each C on the double bond

E.g. the cis-trans isomers of but-2-ene



The two identical groups above are the H atoms. When both H atoms are on the same side of the double bond it is called the **cis** isomer. When they are on opposite sides of the double bond it is the **trans** isomer. Geometric isomers may differ in physical and chemical properties.

Optical Isomerism

Optical isomers have the ability to rotate a plane of polarized light. They are referred to as **optically active** compounds.

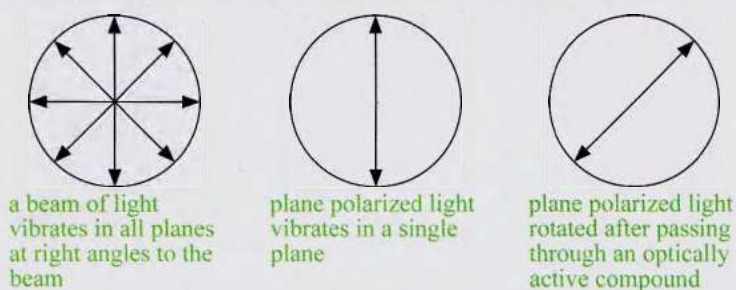


Fig. 18.5 Rotation of a plane of polarized light.

When an optically active compound is placed in a polarimeter, it



can either rotate a plane of polarized light to the right (clockwise) or to the left (anticlockwise). The compound that causes clockwise rotation is called the dextrorotary or D isomer and carries the symbol (+), while the one which causes anticlockwise rotation is called the laevorotary or L isomer and carries the symbol (–).

An organic compound which displays optical isomerism is said to be **chiral**. A chiral compound has no plane, axis or centre of symmetry. It must possess at least one **asymmetric carbon atom**, that is, a carbon atom which has four different groups attached to it. A compound with one asymmetric or chiral carbon has two isomers which are non-superimposable mirror images of each other. These non-superimposable mirror images of each other are referred to as **enantiomers**. For example, $\text{CH}_3^*\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ has an asymmetric or chiral $^*\text{C}$ atom and has two optical isomers as shown below in Fig. 18.6.

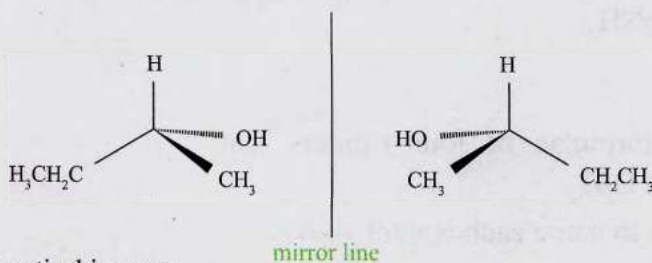


Fig. 18.6 optical isomers

The number of optical isomers a compound has depends on the number of asymmetric or chiral carbons in the compound. A compound with n chiral carbons has 2^n number of isomers. Another example is lactic acid, $\text{CH}_3^*\text{CH}(\text{OH})\text{COOH}$. The (+) form can be extracted from animal muscle. The (–) form does not occur naturally.

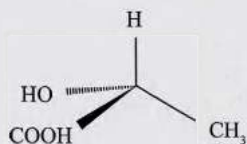


Fig. 18.7 Lactic acid

A sample which contains a chiral carbon atom and is optically inactive is called a **racemic mixture**. This implies that there is a 1:1 ratio of the D and L isomer existing in the sample so that the rotation of the plane of polarized light to the left cancels the rotation to the right and the net rotation equals zero. Laboratory preparation of an optically active compound from optically inactive materials gives a racemic mixture. Optical isomers show similar physical and chemical properties.





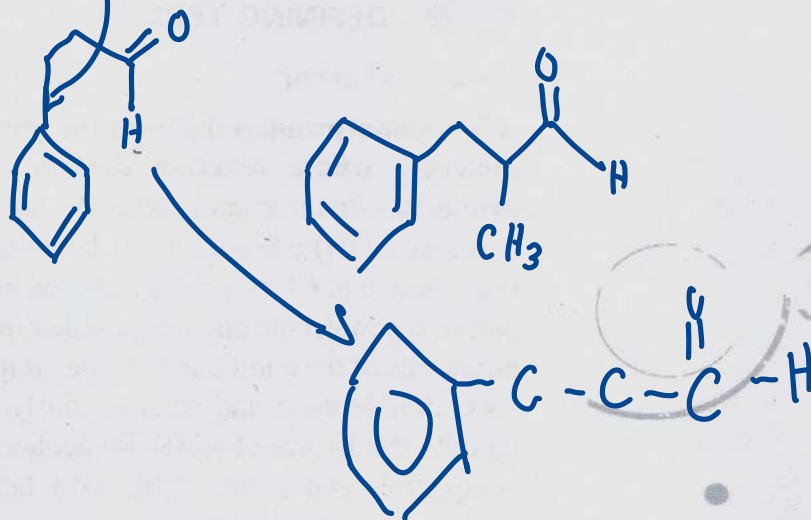
Questions

1.
 - (a) Define the term *structural isomerism*.
 - (b) Name the type of structural isomerism shown by each pair of compounds given below.
 - (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CHOHCH}_3$
 - (ii) $\text{CH}_3\text{CH}_2\text{CHO}$ and CH_3COCH_3
 - (c) Define the term *stereoisomerism*.
 - (d) Name the type of stereoisomerism shown by each compounds given below.
 - (i) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$
 - (ii) CHBrCHBr
2.
 - (a) Draw the displayed formulae of four isomers that conform to the formula C_4H_8 .
 - (b) Use the IUPAC system to name each isomer above.
3. Combustion analysis of 1.0 g of a compound containing only carbon, hydrogen and oxygen gives 2.3 g of carbon dioxide and 0.93g of water. If the relative molecular mass of the compound is 58, calculate the empirical and molecular formula of the compound.
4. Using the compound of molecular formula $\text{C}_4\text{H}_8\text{O}_2$, illustrate the following types of isomerism.
 - (a) chain isomerism
 - (b) positional isomerism
 - (c) functional group isomerism
5. 2-hydroxypropanoic acid obtained from sour milk rotates a plane of polarized light.
 - (a) Draw the structural formula of 2-hydroxypropanoic acid and explain why it can rotate a plane of polarized light.
 - (b) Explain why laboratory preparation of this acid shows no optical activity.



6. Draw the structural formula for the following compounds:

- (a) 2-chloropropanoic acid
- (b) 2,2-dimethylpropane
- (c) *cis*-but-2-ene
- (d) cyclopentene
- (e) 1,2-diethylbenzene
- (f) 4-bromophenol
- (g) 2-methylbutan-2-ol
- (h) Phenylethanol
- (i) 3-methylbutanone
- (j) 3-phenylpropanal
- (k) Propanonitrile
- (l) Propyl benzenecarboxylate



The mechanism of an organic reaction gives the details of all stages in the reaction, highlighting the electron movements as well as all species that are generated within the reaction. Organic reaction mechanisms are of different types depending on the kind of reactions that are taking place as well as the homologous series that is undergoing the reactions. At this time it is necessary to define a few terms that will occur frequently in the description of the reaction.



DEFINING TERMS

Functional group

A functional group is that atom or group of atoms in an organic molecule whose reaction determines its overall chemical properties. In the organic acids the functional group is a group of atoms (COOH) whereas in the haloalkanes the functional group is an atom e.g. Cl. It is the functional group which is the reactive part of the molecule and hence it determines the overall chemical properties of the compound. For example, all alkenes contain the C=C double bond and react similarly. Other functional groups include the hydroxyl (OH) in alcohols, the (C=O) in carbonyl compounds and esters. Table 19.1 below gives a list of some common functional groups.

Table 19.1 Some common functional groups

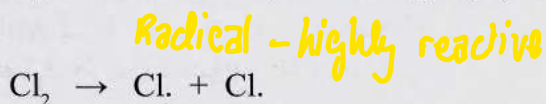
Homologous series	General formula	Functional group
Alkanes	C_nH_{2n+2}	
Alkenes	C_nH_{2n}	C = C
Alkynes	C_nH_{2n-2}	C $\equiv$ C
Alcohols	$C_nH_{2n+1}OH$	OH
Carboxylic acids	$C_nH_{2n+1}COOH$	COOH
Esters	$C_nH_{2n+1}COOC_nH_{2n+1}$	COO
Aldehydes	$C_nH_{2n+1}CHO$	CHO
Ketones	$C_nH_{2n+1}COC_nH_{2n+1}$	C=O
Nitriles	$C_nH_{2n+1}C\equiv N$	C $\equiv$ N

Homolytic fission

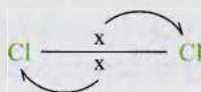
Homolytic fission is the symmetrical splitting of a bond in which each atom takes an equal share of the bonding electrons



forming free radicals. For example, the chlorine molecule (Cl_2) splits homolytically in the presence of ultraviolet light to give two identical chlorine radicals. This process is called homolysis. Each chlorine free radical has one electron from the shared pair. Homolytic fission usually occurs in non-polar or slightly polar bonds.



In this mechanism, single headed arrows are used to show single electron movement.



Free radicals are very reactive species because the unpaired electron that was previously bonded has not yet returned to its low energy ground state.

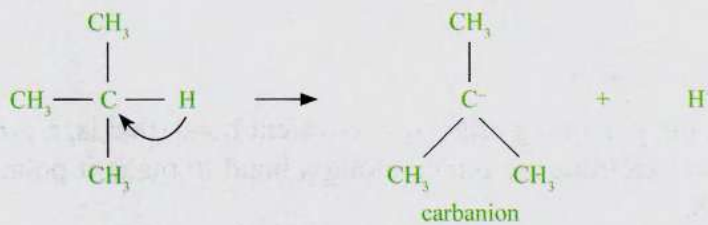
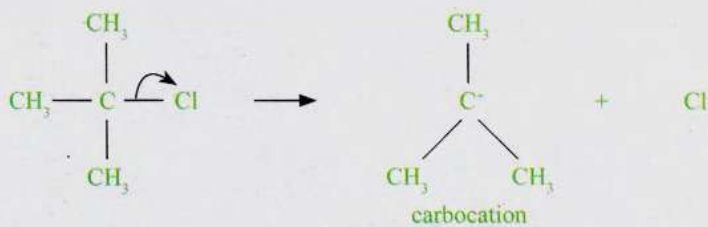
Heterolytic fission

Heterolytic fission is the unsymmetrical breakage of a covalent bond resulting in charged species of opposite poles.

This usually occurs in polar bonds when the two electrons are pulled in one direction due to the presence of an electronegative element. The electrons are not evenly shared and therefore go towards the more electronegative element.



Note that full headed arrows are used to show the movement of the two electrons. In heterolytic fission an anion and a cation are formed. When a positively charged carbon atom is formed it is called a **carbocation** or **carbonium ion**. When a negatively charged carbon atom is formed it is called a **carbanion**.



Electrophiles

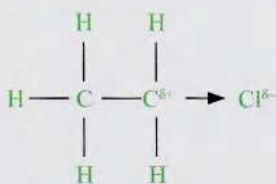
These are electron deficient species usually carrying a positive charge (i.e. electron-seeking reagents). They are usually very reactive and attack a region of high electron density. They will accept a pair of electrons to form a dative bond in an organic molecule. Electrophiles are generated within a reaction mixture (in situ) and cannot be isolated e.g. NO_2^+ and Br^+ .

Nucleophiles

These are the opposite of electrophiles. They are electron rich species which attack positively charged centers (i.e. nucleus seeking reagents). They do not necessarily carry a negative charge but must contain at least one lone pair of electrons to donate to an electron deficient atom to form a dative bond e.g. Cl^- and NH_3 . Ammonia contains a lone pair of electrons in the p orbital and this lone pair is readily available for the formation of a dative covalent bond, making it an excellent nucleophile.

Polar Covalent Bond

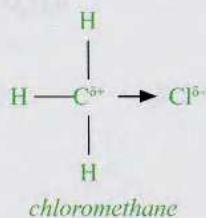
This is a covalent bond formed by the sharing of a pair of electrons between two atoms which differ in electronegativity. Electronegativity is the ease with which an atom attracts the electron pair in a covalent bond. If one of the atoms is more electronegative and pulls the electron density closer towards itself, then there will be uneven sharing of the electron density. This allows the adjacent atom to be relatively bare of the electron pair. As a result, the bond has a partial positive charge at the less electronegative end and a partial negative charge at the more electronegative end. A covalent bond containing charge dispersion (difference) like this is said to be polar covalent. For example,



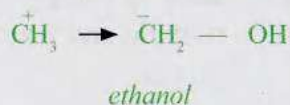
The Cl atom pulls the electrons away from the carbon atom to which it is directly attached creating charge differences in the molecule. As such the molecule is said to be a polar covalent compound.

Inductive Effect

This is the polarizing effect of a covalent bond, that is, a process whereby electrons are pulled along a bond to make it polar. For example,



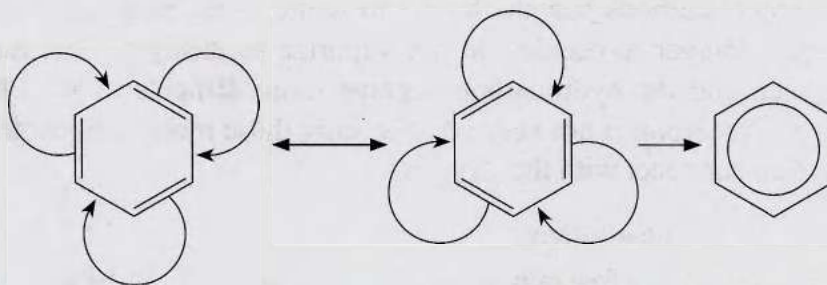
The chlorine atom is an electron withdrawing species which pulls electrons away from the carbon atom as shown in chloromethane. Thus Cl is said to have a **negative inductive effect (-I)** on the bond.



Methyl groups tend to be electron donating and push the electron density towards the carbon atom as shown in ethanol. Thus CH_3 is said to have a **positive inductive effect (+I)**.

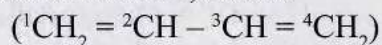
Conjugative Effect

This occurs where there are alternating double and single bonds in a molecule such as in benzene. The electrons are free to move in the available p orbitals of the ring system and are said to be delocalized, that is, the electrons are not in one particular place but are in constant continual motion. This results from the sideways overlap of the p orbitals which creates π bonds. This gives additional stability to the benzene molecule.



The electrons are free to move and their movements are shown by the arrow. These structures are called resonance structures and the double headed arrow shows that both structures can exist. The benzene ring is therefore shown with a circle inside as a simplified structure in which the circle represents resonance of electrons.

Also in molecules such as but-1,3 diene



there is a considerable degree of delocalization. The p orbitals which overlap to form the $\text{C}=\text{C}$ between the 1-2 and 3-4 carbon atoms can also overlap between 2-3 atoms.



ALKANES

Alkanes are saturated hydrocarbons which have the general formula $\text{C}_n\text{H}_{2n+2}$. They contain only strong $\text{C}-\text{C}$ and $\text{C}-\text{H}$ bonds which make them relatively inert. Therefore their chemistry is restricted to reactions that can overcome the high activation energy

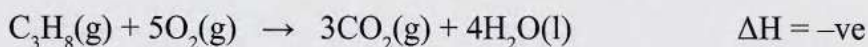


required to break the C – C and C – H bonds. Combustion and free radical substitution reactions can provide the energy required to break these bonds and force alkanes to undergo reactions.

Reactions of alkanes

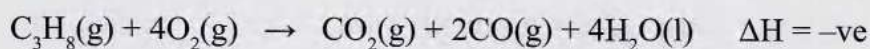
Combustion

The combustion of alkanes is an important source of energy for man. Alkanes burn in oxygen to form carbon dioxide and water. The equation below shows the combustion of propane.



You will observe that all of the covalent bonds in the propane molecule have been broken and an entirely new set of covalent bonds is formed in the products.

If there is an insufficient supply of oxygen, the products will consist of carbon monoxide, a highly toxic gas.

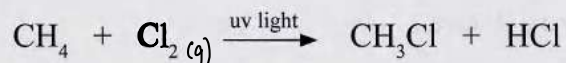


The hydrocarbons become harder to ignite as the molecules get bigger. Bigger molecules do not vaporize so easily so that the oxygen and the hydrocarbon become more difficult to mix. If the hydrocarbon is not very volatile, only those molecules on the surface can react with the oxygen.

Free radical substitution

Alkanes undergo free radical substitution reactions with halogens. In these reactions, the halogen forms free radicals which substitute one or more hydrogen atoms of the alkane. The mechanism of this reaction takes place in three steps known as **initiation**, **propagation** and **termination**.

The halogenation of an alkane appears to be a simple substitution reaction in which a C-H bond is broken and a new C-X bond is formed. The chlorination of methane is shown below as an example of this reaction.



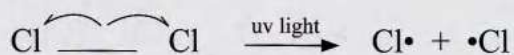
Initiation

Homolytic fission is the first step in which the chlorine molecule is broken by UV light to produce two identical radicals. A radical is an atom with an unpaired electron and has a lot of energy, therefore it is very reactive.



Propane gas lighting is efficient and reliable

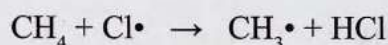




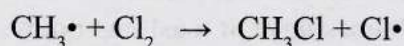
photochemical homolysis of Cl_2

Propagation

This involves two steps. First the chlorine radical reacts with a methane molecule to generate the methyl radical and hydrogen chloride. Then the methyl radical reacts with a Cl_2 molecule to regenerate the chlorine radical. This chlorine radical goes on to take part in another propagation reaction causing a chain reaction.

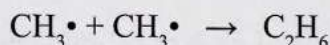
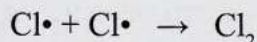


Free radical substitution at methyl groups

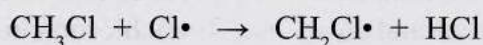


Termination

This involves recombination of two free radicals. This can happen in three ways:



Further substitution can occur where all the H atoms can be replaced by chlorine. The relative amounts of the various products depend on the proportion of the two reactants used. Excess Cl_2 give rise to further substitution.

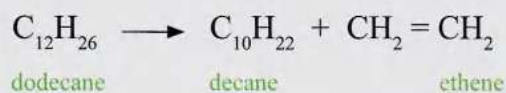


The rate of halogenation varies with the different halogens. The reactivity of alkanes with fluorine is too fast to control, that with chlorine and bromine is moderate, while the reaction with iodine is too slow to be of practical use.

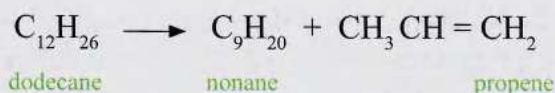
Cracking

Alkane molecules are cracked into smaller molecules. The cracked products may be smaller alkanes, alkenes and hydrogen molecules. The large hydrocarbon molecule can break anywhere along the carbon chain to form a variety of smaller molecules. For example, dodecane can break into decane and ethene





or nonane and propene.



Cracking is carried out either using heat or a catalyst (see pages 423-424).



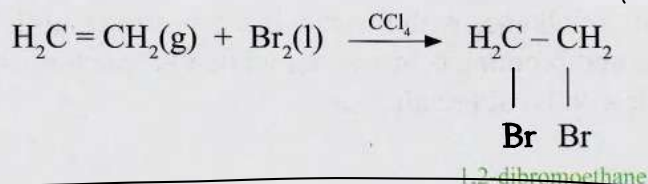
ALKENES

Alkenes are unsaturated compounds which have the general formula C_nH_{2n} . Alkenes have at least one double bond consisting of a sigma and a pi bond between two carbon atoms. Although the double bond between two carbon atoms is a stronger link than a single bond, the pi bond is more vulnerable to attack by suitable reagents. Thus alkenes tend to undergo addition reactions where the unsaturated carbon atoms become saturated.

Reactions of alkenes

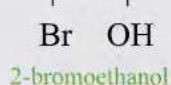
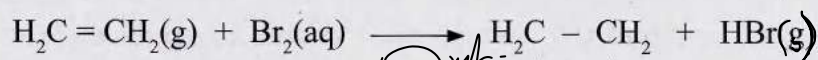
The halogenation of alkenes

Alkenes decolourize a solution of bromine in an organic solvent. Alkenes react with bromine decolourizing the bromine to produce an oily addition compound. A bromine atom each becomes attached to the two carbon atoms bearing the double bond. The mechanism of this reaction is electrophilic addition. This reaction is of particular significance since it is used as a test to distinguish between an alkane and an alkene. Tetrachloromethane (CCl_4) is a common solvent used since it is non-polar and will dissolve both the bromine and the alkene. It is also inert and does not take part in the reaction.



Alkenes also decolourize aqueous bromine however different products are formed. For example, ethene reacts with aqueous bromine to form 2-bromoethanol and hydrogen bromide.

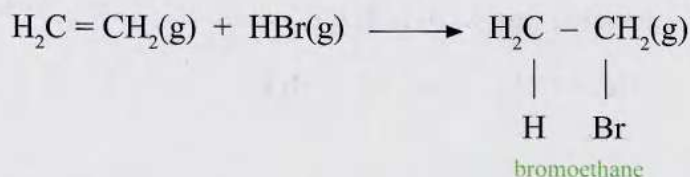




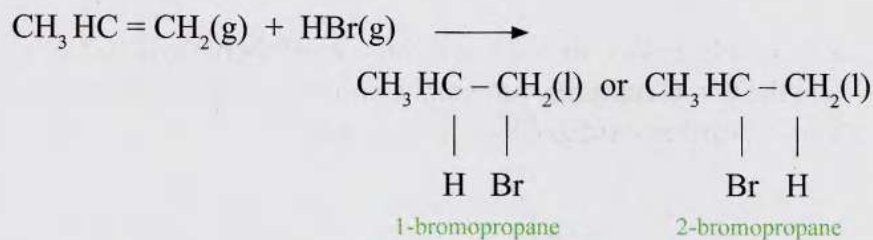
addition but
no substituted
alcohol

Hydrohalogenation of alkenes

The hydrogen halides HCl, HBr and HI can all be added across the double bond of alkenes. For example, ethene reacts with hydrogen bromide to form bromoethane.



When the alkene molecule is unsymmetrical, two possible products can be formed. For example, the addition of hydrogen bromide to propene can form either 1-bromopropane or 2-bromopropane.



The major product in this reaction is found to be 2-bromopropane. Markovnikov, a Russian chemist formulated a rule to predict which product will be dominant when a hydrogen halide is added to an unsymmetrical alkene. This rule is called **Markovnikov's rule**. It states that when a compound HX is added to an unsymmetrical alkene, the H becomes attached to the unsaturated carbon which has the larger number of hydrogen atoms. Therefore in the reaction above, the H is attached to the CH_2 group and not the CH group.

The oxidation of alkenes

Alkenes are oxidized by powerful oxidizing agents such as potassium manganate (VII) to form a variety of products depending on the conditions chosen.

Hot, concentrated, acidified KMnO_4

In the presence of hot, concentrated, acidified KMnO_4 , the double bond of the alkene is broken and a variety of products is produced depending on the alkene used. As a general rule

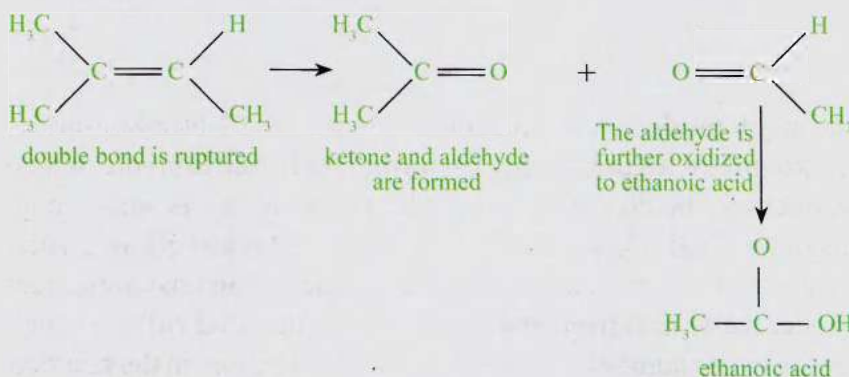


- terminal CH_2 groups are oxidized to produce carbon dioxide and water.
- an aldehyde produced is further oxidized to the corresponding carboxylic acids.
- ketones produced are not further oxidized since they are stable.

For example, when propene is oxidized with hot, concentrated, acidified KMnO_4 , the $\text{C}=\text{C}$ double bond is broken. The terminal CH_2 group is oxidized to carbon dioxide and water while the aldehyde ethanal is further oxidized to ethanoic acid.

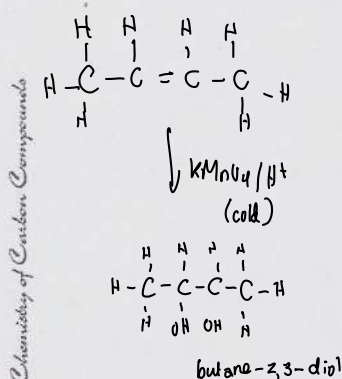
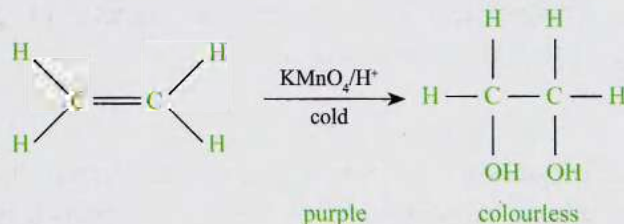


The example below shows the oxidation of 2-methylbut-2-ene. When the $\text{C}=\text{C}$ ruptures, propanone and ethanal are formed. The ethanal is further oxidized to ethanoic acid.



Cold acidified KMnO_4

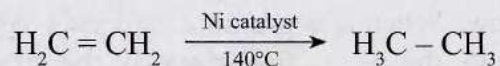
Cold acidified potassium manganate (VII) oxidizes an alkene to a diol. For example ethene is oxidized to ethane-1,2-diol.



The colour of the solution changes from purple to colourless as the oxidation state of manganese in the MnO_4^- ion is reduced from +7 to +2.

The hydrogenation of alkenes

Alkenes undergo hydrogenation to produce the corresponding alkane. There is a change from an unsaturated compound to a saturated compound.

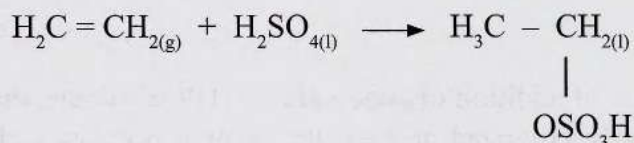


Fat usually contains unsaturated fatty acids. Unsaturation in fat leads to lower melting points and as such they exist as liquids due to existence of less van der Waals forces of attraction between the molecules. Liquid vegetable oils are not stable to heat and can go rancid easily. Therefore hydrogenation of the double bond in cheap fats such as cottonseed oil, corn oil and soya bean oil converts liquids into solids having the same constituency comparable to that of lard and butter. This is called the “**hardening**” of fats. Saturated fats can withstand the temperatures of food production processes and reduce rancidity so providing a better shelf life. The rancidity of fats occurs because oxygen attacks the double bond portion of the unsaturated fat. Hydrogenated fats lack double bonds therefore they do not become rancid.

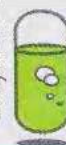
In nature, most unsaturated fatty acids are cis-isomers. However, during the process of hydrogenation of either vegetable or fish oils some cis-isomers are converted to trans-isomers. Fats containing trans-isomers are called **trans fats**. Researchers have found that trans fats increase cholesterol which may increase the risk of heart disease. In addition, trans fats are associated with some types of cancer.

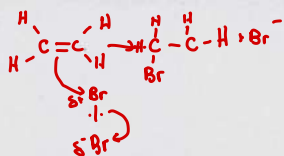
Hydration of alkenes

Alkenes can be hydrated to alcohols using concentrated sulphuric acid. For example, ethene reacts with concentrated sulphuric acid at room temperature to form ethyl hydrogensulphate.



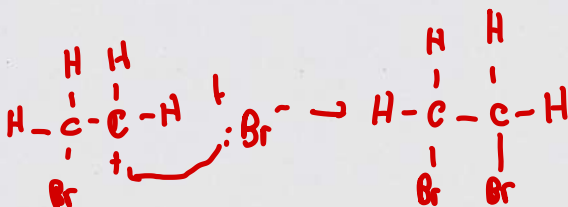
When ethyl hydrogensulphate is warmed with water, it is hydrolysed to ethanol.



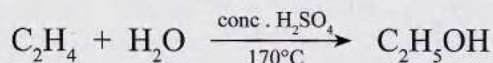


Reagents that are reacted with alkenes as the molecules approach there is repulsion

Step 2 :

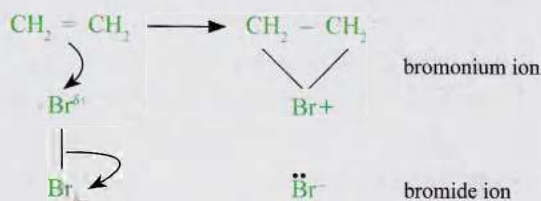


The overall equation for the reaction is

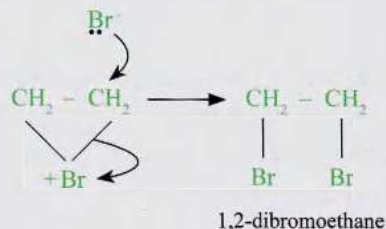


Electrophilic addition

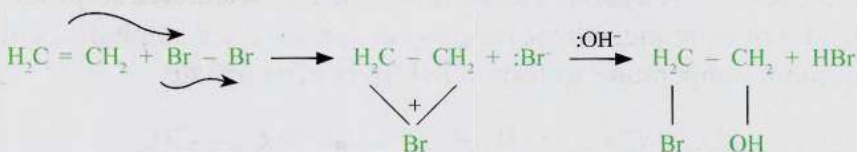
The proposed mechanism for the addition of bromine to alkenes is **electrophilic addition**. For example the mechanism for the reaction of ethene with bromine in an organic solvent e.g. CCl_4 is shown below. When the bromine molecule approaches the ethene molecule, the pi electron cloud in the ethene molecule polarizes the bromine molecule. Further polarization results in the formation of a bromonium ion and a bromide ion.



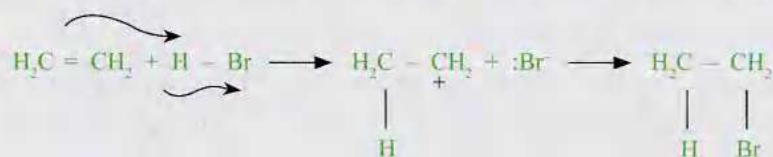
The bromonium ion is attacked by the bromide ion to form 1,2-dibromoethane. Bromine is red brown in colour and goes colourless as it is used up. The reaction takes place readily at room temperature in the laboratory.



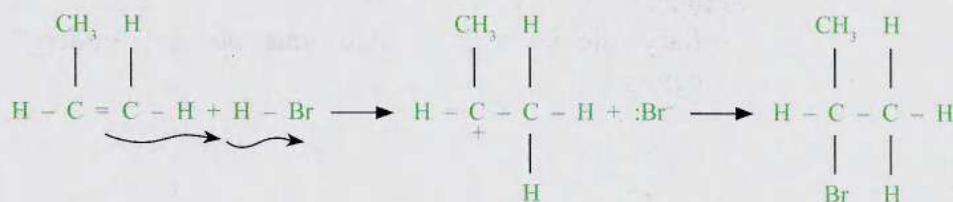
In reactions with aqueous bromine, the bromonium ions react with hydroxide ions to give the major product 2-bromoethanol and hydrogen bromide. A minor product of 1,2-dibromoethane is formed with the bromide ions.



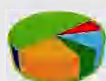
In the case of addition of concentrated HBr to ethene, the HBr is permanently polarized and ethene forms a primary carbocation instead of a bromonium ion.



If alkenes are not symmetrical e.g. propene, the H adds to the C which has the more H atoms (Markovnikov rule). The major product is the one in which the more stable carbocation is formed.

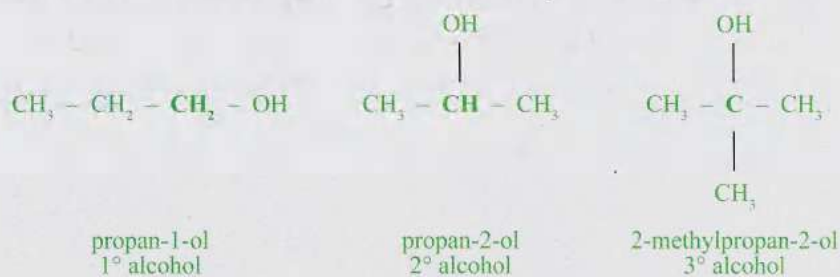


The intermediate carbocation formed is secondary. This is more stable than the primary carbocation which would have formed if the hydrogen became attached to the carbon with less hydrogen atoms.



ALCOHOLS

Alcohols have the general formula $\text{C}_n\text{H}_{2n+1}\text{OH}$. The functional group of the alcohols is the hydroxyl group (OH). This group has two reactive covalent bonds, the C-O bond and the O-H bond, since the electronegativity of oxygen is greater than that of carbon and hydrogen. Alcohols are classified on the basis of the number of carbon atoms which are bonded directly to the carbon which is attached to the OH group. In **primary (1°) alcohols**, the OH is attached to a carbon which is bonded to one other carbon. In **secondary (2°) alcohols**, the OH is attached to a carbon which is bonded to two other carbons. In **tertiary (3°) alcohols**, the OH is attached to a carbon which is bonded to three other carbons.

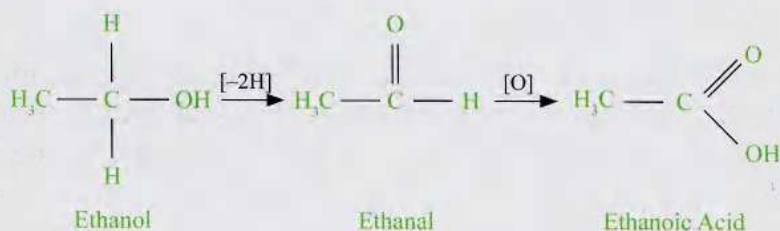


The oxidation of alcohols

Oxidizing agents such as potassium manganate(VII) and potassium dichromate(VI) can be used to distinguish between primary, secondary and tertiary alcohols.

- Primary alcohols are oxidized to aldehydes, which are unstable and are further oxidized to the corresponding carboxylic acid.
- Secondary alcohols are oxidized to the corresponding ketone.
- Tertiary alcohols are stable and do not undergo oxidation.

Primary alcohols $\longrightarrow$ *aldehydes* $\longrightarrow$ *carboxylic acids*



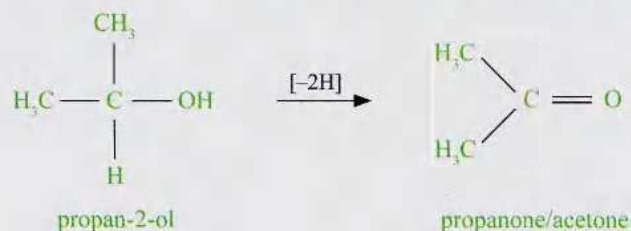
Acidified potassium dichromate(VI) will oxidize primary alcohols to aldehydes at room temperatures. At higher temperatures, it will oxidize the primary alcohols to carboxylic acids.

Acidified potassium manganate(VII) is a very powerful oxidizing agent and does not stop at the aldehydes stage in primary alcohols, it oxidizes straight to carboxylic acids.

Breathalyzer test

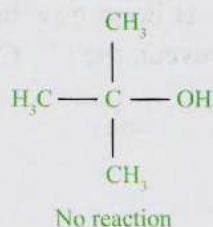
The breathalyzer test is used to determine if a driver is intoxicated. The driver is asked to exhale into a vessel containing potassium dichromate. If he has consumed alcoholic drinks, the ethanol from his breath is oxidized to the corresponding acid. The $\text{Cr}_2\text{O}_7^{2-}$ ion which is orange is reduced to the Cr^{3+} ion which is green. The oxidation number of chromium changes from +6 to +3. Thus, if a driver is drunk, there is a change of colour from orange to green.

Secondary alcohols $\longrightarrow$ *Ketone (no further reaction)*



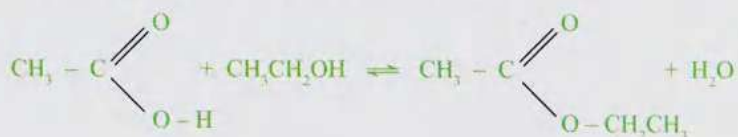
If acidified potassium manganate (VII) is used with the primary or secondary alcohol, the colour change would be from purple to colourless as the MnO_4^- ion is reduced to the Mn^{2+} ion.

Tertiary alcohol $\rightarrow$ *No reaction, stable towards oxidation*



Esterification

Alcohols react with carboxylic acids to form sweet smelling compounds known as esters. The reaction involves heating the alcohol and the carboxylic acid under reflux in the presence of an acid catalyst. The catalyst is usually concentrated sulphuric acid. Heating under reflux prevents loss of the volatile compounds as the vapours are allowed to condense and re-enter the round bottom flask in which the reaction is occurring. Esterification is a condensation reaction, that is, one in which two smaller molecules are joined together to form a larger molecule with the loss of small molecules such as water. The esterification reaction is both slow and reversible. The equation for the reaction between ethanol and ethanoic acid to form ethyl ethanoate is given below.



Alcohols labelled with ^{18}O show that in primary alcohols, the O – H bond of the alcohol is broken in esterification.



Labelled ^{18}O shows up in the ester while none appears in the water. This means that H from the alcohol combines with OH from the acid to form water. Research has shown that in tertiary and some secondary alcohols it is the R – OH bond of the alcohol that is broken.

Dehydration of alcohols

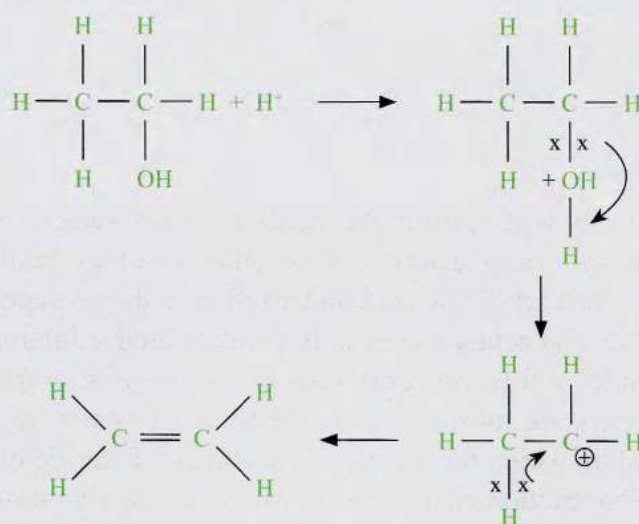
Alcohols undergo dehydration reactions to produce alkenes. Concentrated sulphuric acid is a suitable dehydrating agent and is used to effect this conversion. The initial step in this reaction is



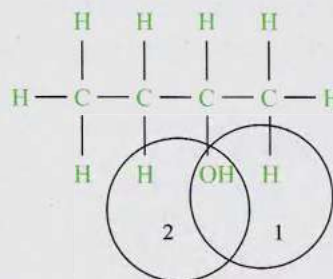
Ethyl pentanoate has a pleasant aroma and taste. It is used as a food additive to give a fruity flavour of apple.



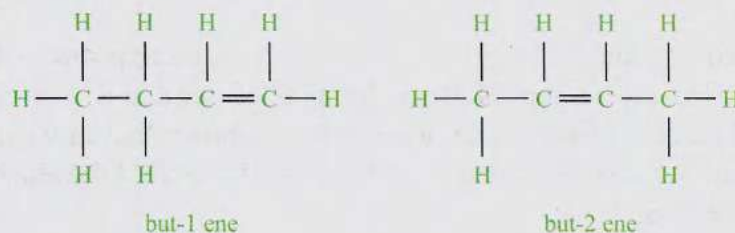
the protonation of the hydroxyl group. The oxygen atom uses its lone pair of electrons to form a dative bond with the H^+ ions and in doing so gains a positive charge. The two electrons constituting the $C - O$ bond now flow onto the positively charged oxygen atom forming water and leaving a positively charged carbocation behind. The adjacent $C - H$ bond now breaks, giving up H^+ and the two electrons flow between the $C - C$ bond forming a π bond producing the double bond.



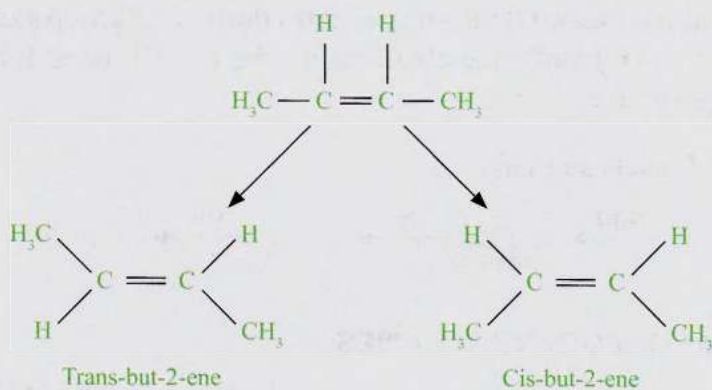
Consider an example in which isomers can be formed



Water can be lost in two ways. In process 1, dehydration produces but-1-ene while process 2, but-2-ene is formed.



But-2-ene can exhibit geometric isomerism and can have two isomers.



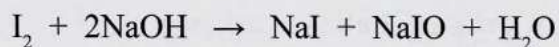
The iodoform reaction NaOH / I_2

The iodoform test is a specific reaction for

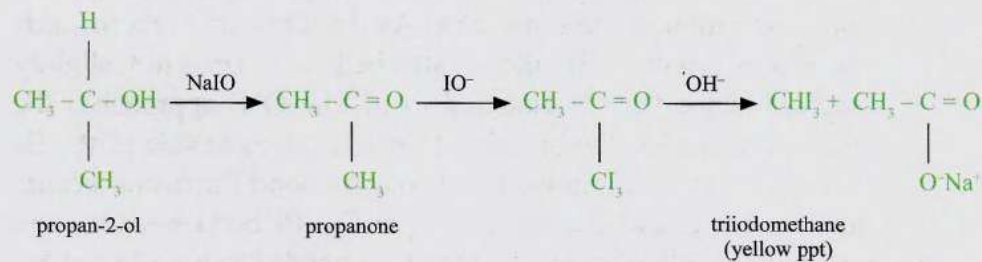
- alcohols of type $\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{OH} \\ | \\ \text{CH}_3 \end{array}$
- ketones of type $\begin{array}{c} \text{CH}_3-\text{C}=\text{O} \\ | \\ \text{R} \end{array}$
- ethanal $\begin{array}{c} \text{CH}_3-\text{C}=\text{O} \\ | \\ \text{H} \end{array}$

The reaction is carried out using aqueous iodine and sodium hydroxide which produces a yellow precipitate of triiodomethane (iodoform).

First, the iodine disproportionates in the aqueous sodium hydroxide to give sodium iodide, sodium iodate (I) and water.

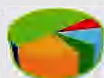


The sodium iodate (I) oxidizes propan-2-ol to propanone.



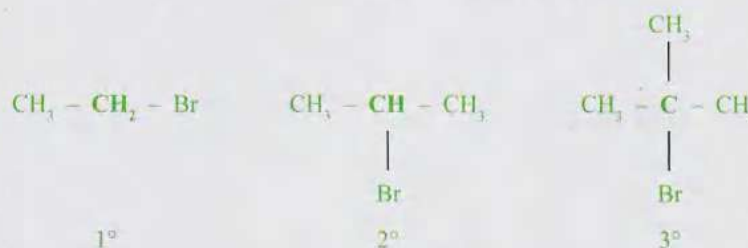
The sodium iodate (I) then halogenates the methyl group attached to the C = O. Finally the alkali breaks the C – Cl₃ bond forming triiodomethane.

Ethanol reacts similarly.



HALOGENOALKANES

Halogenoalkanes are also known as haloalkanes or alkyl halides. These are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine or iodine). Halogenoalkanes are classified on the basis of how the halogen atom is positioned on the carbon chain. In a **primary (1°) halogenoalkane**, the carbon which carries the halogen atom is attached to one other alkyl group. In a **secondary (2°) halogenoalkane**, the carbon to which the halogen is attached to is bonded to two other alkyl groups. In a **tertiary (3°) halogenoalkane**, the carbon to which the halogen is attached to is bonded to three other alkyl groups.

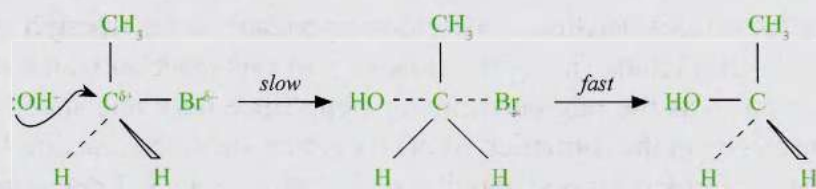


Halogenoalkanes undergo alkaline hydrolysis to produce the corresponding alcohols. The mechanism of these reactions is **nucleophilic substitution**. However the mechanism varies depending on whether the halogenoalkane is primary, secondary or tertiary.

Hydrolysis of primary halogenoalkanes

The mechanism proposed for the hydrolysis of a primary halogenoalkane e.g. bromoethane involves bond breakage and bond formation at the same time. As the electron shifts towards the electronegative Br, the C attached to it becomes slightly positive hence OH⁻ is attracted to it. The OH⁻ approaches the carbon attached to the bromine from the opposite side of the Br atom in order to minimize repulsion. As bond formation occurs between the C and O of the OH⁻, the C – Br bond weakens and a transition state is reached where C is bonded to both O and Br. The transition state is then quickly converted into products.





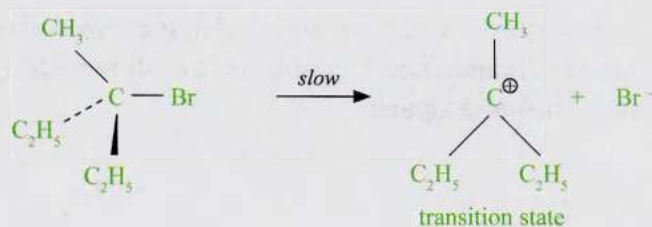
A pentavalent C atom is present here. This is the activated complex in which bond breakage and bond formation is occurring at the same time.

Since two species are involved in the formation of the transition state, the reaction is called bimolecular nucleophilic substitution or an S_N2 reaction. Primary halogenoalkanes undergo S_N2 reactions.

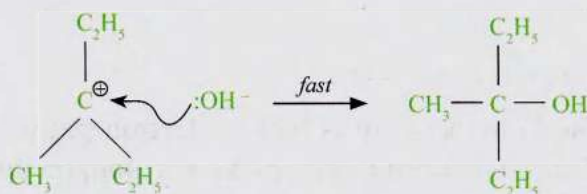
If the halogenoalkane has a chiral C atom, then the hydrolysis product would be the corresponding optical isomer since the OH^- attacked from the opposite direction. This is called **reversal of configuration**.

Hydrolysis of tertiary halogenoalkanes

The mechanism proposed for the hydrolysis of a tertiary halogenoalkane e.g. 3-bromo-3methylpentane involves the dissociation of the halogenoalkane into a carbocation and a halide ion. The trigonal planar carbocation is stabilized by the electron donating alkyl groups.



Then the carbocation quickly reacts with the hydroxide ion to form an alcohol.



The OH^- ion can attack above or below the plane of the flat trigonal intermediate. If the C atom is chiral, then there is equal probability both the D and L isomer being formed. This means that a 1:1 isomer mixture is produced, that is, a racemic mixture in which the optical rotation is equal to zero.



The rate of this reaction is therefore dependant on the strength of the C – Hal bond. This is the slow step of this reaction which is referred to as the rate-determining step. Since only one species is involved in the formation of the transition state, the reaction is called unimolecular nucleophilic substitution or an S_N1 reaction. Tertiary halogenoalkane produce the more stable tertiary carbocation and hence undergo S_N1 reactions.

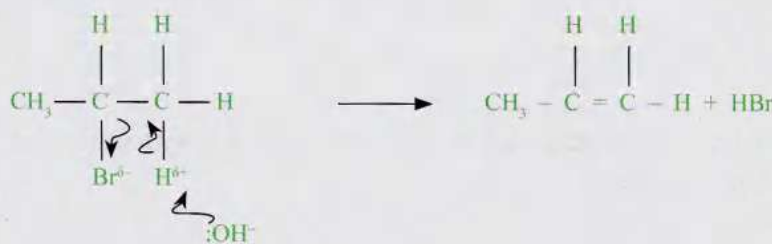
Secondary halogenoalkane

Secondary halogenoalkanes show intermediate behaviour between primary and tertiary halogenoalkane. They can take part in both S_N1 and S_N2 reactions depending on the nature of the halogenoalkane.

Elimination mechanism

When halogenoalkanes undergo reactions with bases, nucleophilic substitution and/or elimination reactions can occur. When halogenoalkanes react with strong bases such as the hydroxide anion (OH^-), a mixture of both products is usually formed. The major product depends on the reaction conditions and the structure of the molecule. Elimination reaction is favoured by strongly basic reagent in a non-aqueous solvent such as ethanolic potassium hydroxide (KOH / ethanol). Secondary or tertiary halogenoalkane favour elimination reactions.

Elimination reactions are commonly used in the removal of H – X from a halogenoalkane. The example below shows the removal of HBr from 2-bromopropane.



The mechanism is as follows

- The bromine atom is highly electronegative and pulls electrons toward it. The hydrogen atom on the adjacent carbon atom becomes acidic and labile and can be easily removed by the base (OH^-).
- As the H^+ is removed the two electrons constituting the C – H bond flows inward to form a pi bond between the carbon atoms.
- As the C=C forms, the C-Br bond is broken and the two

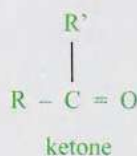
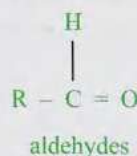
electrons constituting this bond flows onto the bromine atom creating a bromide anion which leaves.

- The net loss is an H^+ and a Br^- which is called dehydrohalogenation.



CARBONYL COMPOUNDS

The carbonyl compounds contain the carbon-oxygen double bond ($\text{C} = \text{O}$) called the carbonyl group. Aldehydes and ketones are two classes of organic compounds that contain the carbonyl group. **Aldehydes contain the carbonyl group which has at least one hydrogen atom bonded to the carbonyl carbon.** Aldehydes have the general formula RCHO where R is an alkyl or aryl group. Aldehydes are valued for their characteristic strong fragrance and taste. For example, the smell of vanilla is given off by the aldehyde vanillin.



Ketones contain the carbonyl group which has two carbon atoms bonded to the carbonyl carbon. Ketones have the general formula RCOR' where R and R' are alkyl or aryl groups. Ketones are more stable than aldehydes and thus undergo fewer reactions.

The carbonyl group is found in a variety of products including glucose, acetone, plastics, adhesives and drugs such as aspirin and penicillin. The structural features of the carbonyl group give these compounds their characteristic properties. Aldehydes and ketones undergo both addition and condensation reactions.

Reaction of carbonyl compounds

Addition of hydrogen cyanide (HCN)

Aldehydes and ketones undergo addition reaction with HCN to produce compounds known as hydroxynitriles or cyanohydrins.



Vanilla beans are used to flavour and fragrance foods and beverages.



Carbonyl compounds are used in the manufacture of penicillin.

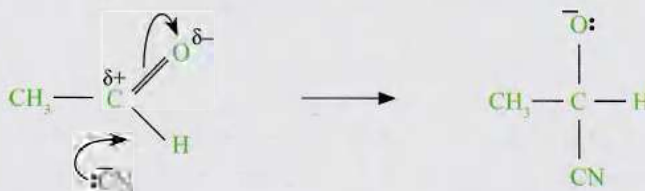




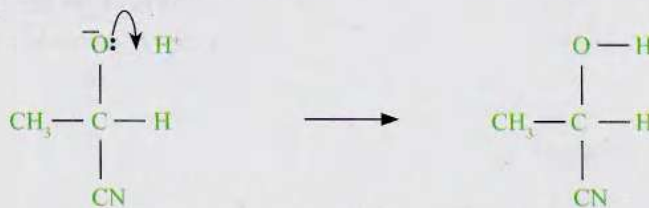
HCN itself is not used in the reaction because it is very toxic. Instead it is generated in the reaction mixture using sodium or potassium cyanide with dilute sulphuric acid. The addition of HCN to a carbonyl compound makes the carbon chain longer by one C atom.

Nucleophilic addition

Nucleophiles are added across the carbonyl group in aldehydes and ketones. The mechanism for the reaction is called **nucleophilic addition**. For example, when HCN is added to ethanal, the HCN dissociates to produce H^+ and the CN^- nucleophile.

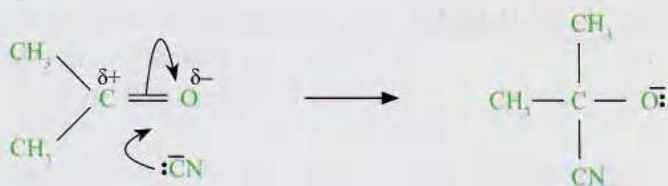


The electronegative O atom in the carbonyl group pulls electron towards itself creating a partial positive charge on the carbon atom of the carbonyl group. The CN^- attacks the partially charged C atom and the pi bond breaks heterolytically with the O atom taking both bonding electrons.

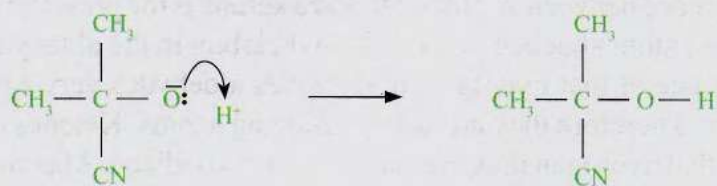


The oxoanion quickly accepts a proton to form 2-hydroxypropanonitrile.

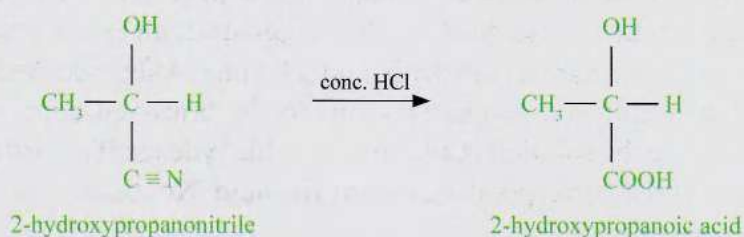
The mechanism is similar for propanone. The slightly positive carbonyl carbon atom is attacked by the cyanide nucleophile.



The pi bond breaks heterolytically with the electronegative O taking both bonding electrons. The oxoanion quickly accepts a proton to form 2-hydroxy-2-methylpropanonitrile.

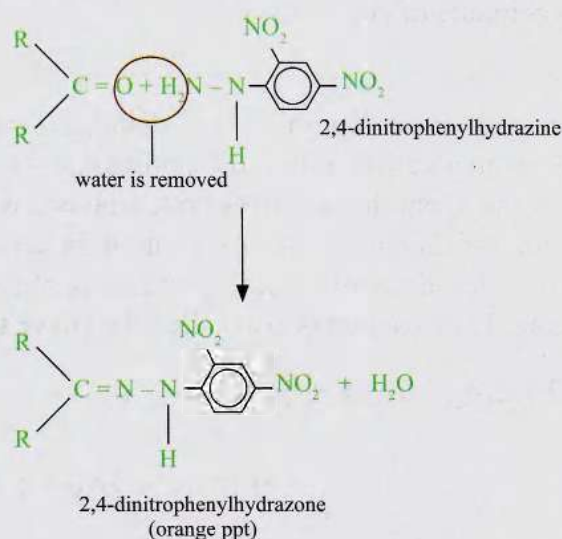


The nitrile group can easily be hydrolysed to the carboxylic group.



Condensation reaction with 2,4-DNPH

2,4-Dinitrophenylhydrazine (2,4-DNPH) also known as Brady's reagent is a suitable reagent used to detect carbonyl compound. When 2,4-DNPH reacts with a carbonyl compound an orange precipitate is produced.



Acetone forms an orange ppt. with 2,4-DNPH.



The reaction is an example of a condensation reaction in which two small molecules combine with the elimination of a molecule of water. The product is known as a 2,4-dinitrophenylhydrazone. The product from the reaction with ethanal would be called ethanal 2,4-dinitrophenylhydrazone. That from propanone would be called propanone 2,4-dinitrophenylhydrazone. Both aldehydes and ketones give a positive test with 2,4-dinitrophenylhydrazine.

Reaction with Fehling's solution

The difference between an aldehyde and a ketone is the presence of a hydrogen atom attached to the carbonyl carbon in the aldehyde. The presence of that hydrogen atom makes aldehydes very easy to oxidize. Therefore they are strong reducing agents. Ketones do not have that hydrogen thus they are not easily oxidized. Aliphatic aldehydes are easily oxidized by mild oxidizing agents whereas ketones and aromatic aldehydes are not.

Fehling's solution contains complexed copper (II) ions in an alkaline solution. It is a weak oxidizing agent which can be used to distinguish between an aldehyde and a ketone. Aldehydes reduce the blue complexed copper (II) ions to the brick-red copper (I) oxide. Since the solution is alkaline, the aldehyde itself is oxidized to a salt of the corresponding carboxylic acid. No reaction occurs with ketones.



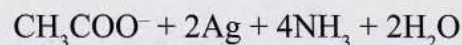
blue solution

brick-red ppt

The equation above shows how ethanal is being oxidized to the ethanoate ion while the blue Cu^{2+} complex ion is reduced to a brick-red precipitate of copper (I) oxide.

Reaction with Tollens' reagent

Tollens' reagent is a complex of diaminesilver (I) ions $[\text{Ag}(\text{NH}_3)_2]^+$ in an alkaline solution. Like Fehling's solution, it is a weak oxidizing agent that oxidizes both aromatic and aliphatic aldehydes but not ketones. The Ag^+ cation is precipitated as metallic silver. The silver forms a silver mirror on the inside walls of the test tube. This reaction is also called the **silver mirror test**.



silver ppt



Propanal forms a silver mirror on the inside wall of the test tube.



The equation above shows how ethanal is being oxidized to the ethanoate ion while the colourless Ag^+ complex ion is reduced to metallic silver.

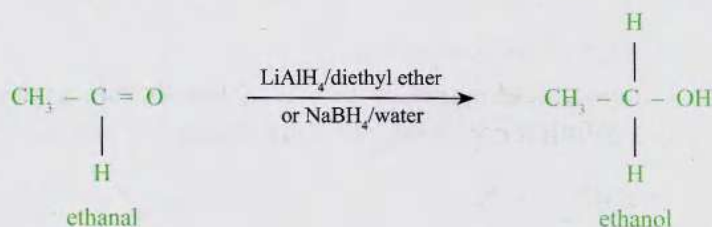
Table 19.1 Fehling's solution and Tollens' reagent can be used to distinguish between aldehydes and ketones.

Carbonyl compound	Brady's reagent	Fehling's reagent	Tollens' reagent
Aldehyde	orange ppt	brick-red ppt	silver mirror on walls of test tube
Ketone	orange ppt	no reaction	no reaction

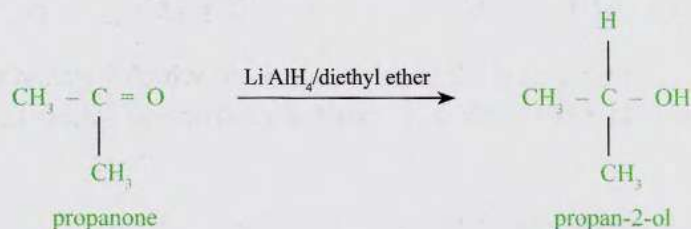
Reduction of aldehydes and ketones

Given the polarization of the carbonyl group, the reagent which adds hydrogen to the electron deficient carbonyl carbon must deliver it as a hydride ion (H^-). Thus aldehydes and ketones are readily reduced with hydride reagents. Reducing agents such as lithium tetrahydridoaluminate (LiAlH_4) and sodium tetrahydridoborate (NaBH_4) act as sources of hydride ions. Aldehydes are reduced to primary alcohols while ketones are reduced to secondary alcohols.

For example, ethanal is reduced to the primary alcohol ethanol.



Similarly propanone is reduced to the secondary alcohol propan-2-ol.



LiAlH_4 is a highly reactive and extremely powerful reducing agent. It is capable of reducing the carbonyl group in aldehydes, ketones and carboxylic acids. NaBH_4 is less reactive and a more selective reagent. It will reduce aldehydes and ketones into

alcohols, but it will not reduce carboxylic acids. Aldehydes and ketones can also be reduced to alcohols with hydrogen gas using a metal catalyst at high temperature and pressure.



CARBOXYLIC ACIDS

Carboxylic acids have the general formula $C_nH_{2n+1}COOH$. The carboxyl group (COOH) characterizes the carboxylic acids. It is made up of a hydroxyl group bonded to a carbonyl group. The change in chemical and physical properties of compounds resulting from the interaction of the hydroxyl and carbonyl group is so profound that it is treated as a distinct and different functional group.

Reaction of carboxylic acids

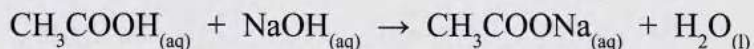
In water, carboxylic acids are proton donors i.e. a hydrogen ion is transferred from the COOH group to a water molecule. The equation below shows ethanoic acid protonating a water molecule.



Thus the reactions of carboxylic acids are similar to those of inorganic acids like hydrochloric acid except they tend to be rather slower.

With metal oxides and hydroxides

If dilute ethanoic acid is mixed with aqueous sodium hydroxide, a colourless solution containing sodium ethanoate is formed.



Similarly ethanoic acid reacts with calcium oxide to form calcium ethanoate and water.

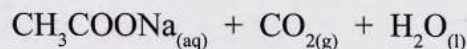
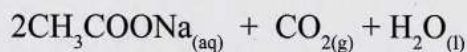
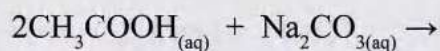


These are simple neutralization reaction in which hydrogen ions from an acid react with hydroxide ions from an alkali to form water.

With carbonates and hydrogencarbonates

Carboxylic acids react with carbonates and hydrogencarbonates to form a salt, carbon dioxide and water. The equations below show the reaction of ethanoic acid with sodium carbonate and sodium hydrogencarbonate respectively.

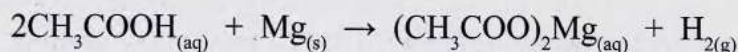




In these reactions effervescence is observed as carbon dioxide is produced. Thus sodium carbonate or sodium hydrogencarbonate can be used as a test to distinguish carboxylic acids from other organic compounds that are weaker acids such as ethanol and phenol.

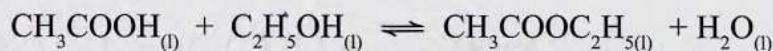
With metals

Carboxylic acids react with the more reactive metals to produce a salt and hydrogen. For example, when magnesium reacts with dilute ethanoic acid, magnesium ethanoate and hydrogen gas is produced



With alcohols

When a carboxylic acid and an alcohol are heated under reflux in the presence of an acid catalyst, an ester is formed. The catalyst is usually concentrated sulphuric acid. The equation for the reaction between ethanoic acid and ethanol to form ethyl ethanoate and water is given below.

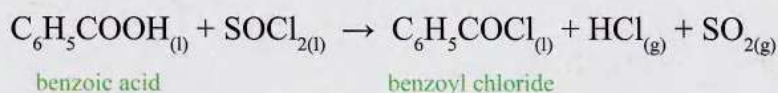
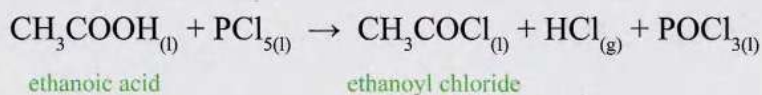


Conversion to acyl chlorides

Powerful halogenating agents displace the $-\text{OH}$ of a carboxylic acid to form an acyl chloride. The acyl chloride is very reactive. This is because two highly electronegative elements are attached to one carbon atom. This leads to the development of a large partial positive charge on the carbon atom which is susceptible to attack by nucleophiles.

Although reagents such as phosphorus pentachloride and phosphorous trichloride are used, the most popular halogenating reagent is thionyl chloride (SOCl_2) also called sulphur dichloride oxide. SOCl_2 is more convenient to produce acyl chlorides since all of the other products are gases. Misty white fumes are formed as the hydrogen chloride makes contact with the air.



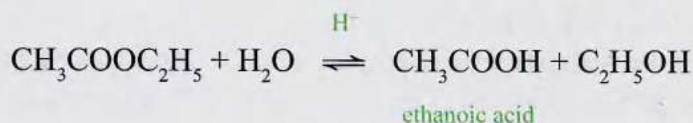


The hydrolysis of esters

There are two ways an ester can be hydrolysed in the laboratory. These are acid hydrolysis and base hydrolysis.

Acid hydrolysis

The reaction is catalyzed by dilute acid. The ester is heated under reflux with dilute hydrochloric acid or sulphuric acid. The ester linkage is broken to form an alcohol and a carboxylic acid.



Since the reaction is reversible, excess dilute acid is added to provide the water to make the hydrolysis as complete as possible.

Base hydrolysis

This is the common way of hydrolysing esters. The ester is heated under reflux with a dilute alkali like sodium hydroxide. Taking the same esters as above, but using sodium hydroxide solution instead of a dilute acid, the following reaction occurs:

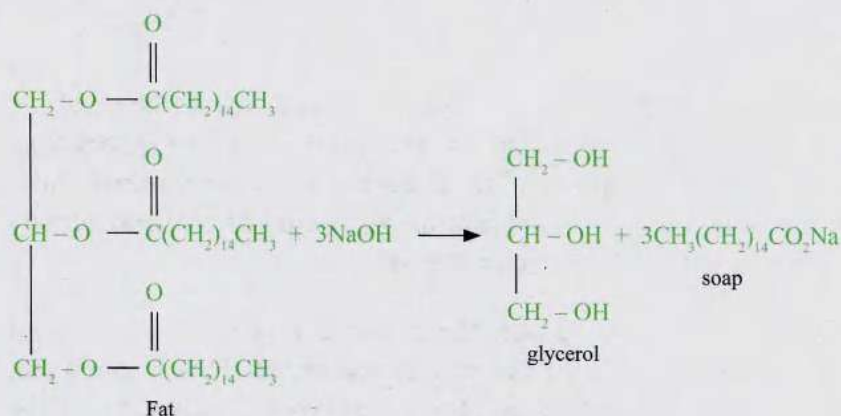


The ester linkage is broken to form the salt of the carboxylic acid and the alcohol. There are two main advantages of doing base hydrolysis rather than using a dilute acid. First the reactions are one-way rather than reversible so the reaction goes to completion. Second the products are easier to separate if all of the ester is hydrolysed.

Saponification

Saponification is the base hydrolysis of natural fats and oils. Fats and oils from plants and animals are natural esters formed from long chain organic acids and propane-1,2,3-triol (glycerol). If animal or vegetable fats and oils are heated with concentrated sodium hydroxide solution, base hydrolysis of the esters occurs.

The products are the sodium salt of the long-chain organic acid (soap) and glycerol.



Transesterification

Transesterification is the conversion of an ester into another ester of that same acid.

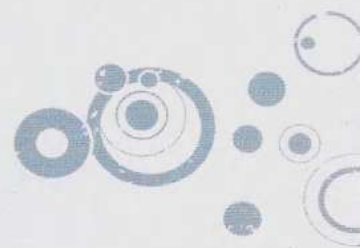


These reactions are often catalyzed by the addition of an acid or base. One of the first uses of transesterified vegetable oil was in making biodiesel which was used to power heavy-duty vehicles in South Africa before World War II.



AROMATIC COMPOUNDS

The most frequently encountered aromatic compound is benzene. The structure of benzene as a six carbon ring with three double bonds was proposed by Kekule. The ring and the three double bonds fit the molecular formula, but the structure did not explain the chemical behaviour of benzene. Each of the double bonds was expected to show the characteristic behaviour of an alkene and undergo addition reactions, but this did not occur in benzene. Kekule suggested that there are two forms of benzene in equilibrium which differ in the positions of the double bonds. But this did not explain the fact that all the carbon-carbon bonds in benzene are the same length. Since the double bonds are separated by single bonds, it means the structure involves conjugation. Therefore an alternative symbol uses a circle inside the hexagon to represent the six π electrons.



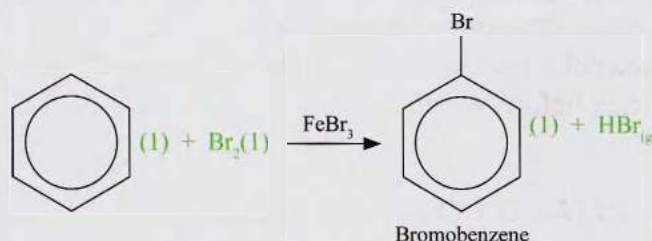


The benzene ring is a highly negative system due to the presence of π electron density which has the ability to move or resonate in the available p orbitals. The electrons are not in one particular position but are in constant motion as a cloud of electron density above and below the plane of the ring.

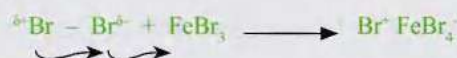
Electrophiles tend to attack the benzene ring system but in all cases the aromaticity of the ring is preserved. This implies that as an electrophile enters, an atom of hydrogen leaves. Since the electrophile is substituting the H in the ring system the mechanism is called **electrophilic substitution**.

Halogenation of benzene

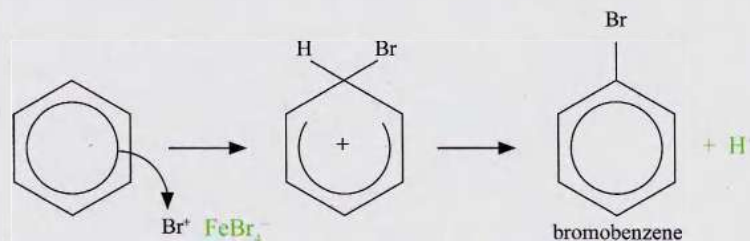
Benzene does not react with halogens on its own. However in the presence of a Friedel-Crafts catalyst, halogenation of benzene takes place at room temperature. A substitution reaction occurs.



A **Friedel Crafts** catalyst (also referred to as a **halogen-carrier**) is a halide such as FeBr_3 or AlCl_3 which has an electron deficient central atom. The central atom can polarize the halogen molecule and accept a pair of electrons from the partial negative halogen atom. For example iron (III) bromide can polarize the bromine molecule and accept a pair of electrons from the partial negative bromine atom. This weakens the Br – Br bond and forms a $\text{Br}^+\text{FeBr}_4^-$ complex.

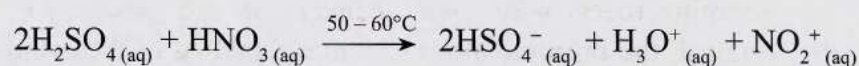


The partially positive bromine atom can now act as the electrophile and attack the pi electrons of the benzene ring system. An intermediate is formed where the bromine bonds to one of the carbon atoms in the ring. Then the intermediate rapidly loses a proton to form bromobenzene.

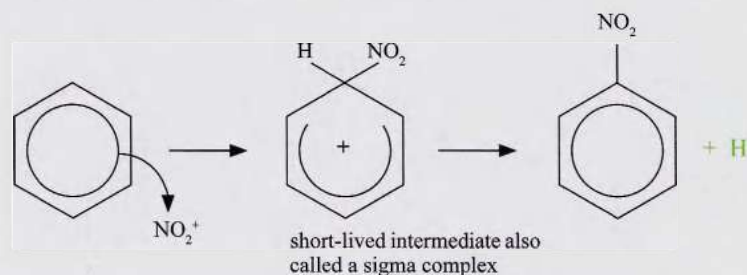


Nitration of benzene

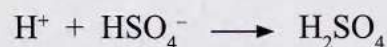
The nitration of the benzene results from the attack of the nitronium ion or nityl cation (NO_2^+). This cation is very reactive and highly unstable and cannot be isolated on its own. Therefore it is generated in situ which means within a reaction mixture. A nitrating mixture is made by mixing concentrated sulphuric and concentrated nitric acid at a temperature of 50 to 60°C.



The nitronium or nityl cation (NO_2^+) is generated in situ. The nitronium or nityl cation (NO_2^+) is then attracted to the delocalized π electrons of the benzene ring. The NO_2^+ cation is added to the ring to form a short lived intermediate.



The symmetry of the delocalized π electrons is disrupted. The ring has lost some of its π electrons and is now electron deficient. Thus the intermediate rapidly loses a proton and the two electrons constituting the $\text{C}-\text{H}$ bond are now donated into the ring to preserve the aromaticity of the ring system. The proton is quickly taken up by the hydrogensulphate ion in solution to form sulphuric acid.

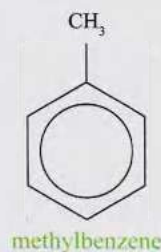


Notice that the sulphuric acid is regenerated and therefore serves as a catalyst in this reaction.

Halogenation of methylbenzene

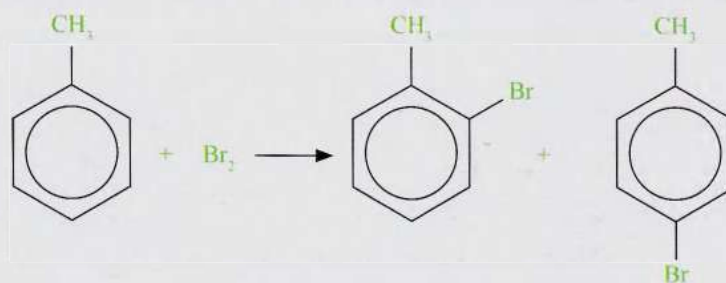
Methylbenzene commonly called toluene is a derivative of benzene in which one of the hydrogen atoms of the ring system has been replaced by a methyl group.





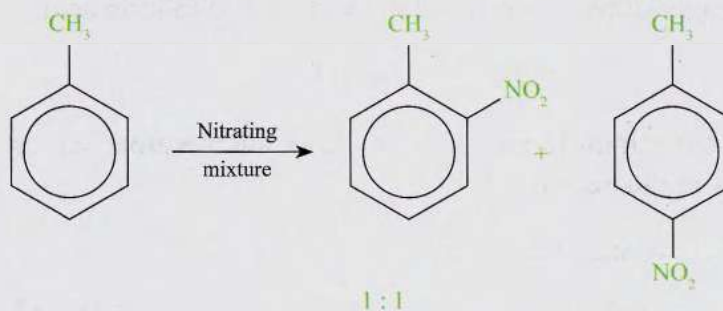
The methyl group on the benzene ring tends to be electron donating and has a positive inductive effect. It pushes the electron density towards the benzene ring system thus activating the ring. This enables electrophilic substitution to occur easier than in benzene. As a general rule activating groups push the incoming electrophile into the 2, 4 and 6 positions. The second and sixth positions are 'ortho' positions while the fourth position is the 'para' position.

When bromine reacts with methylbenzene in the presence of FeBr_3 catalyst, the bromine atom becomes attached to the ortho and para position. Only mono-substituted products are formed at room temperature. There is an equal probability of the bromine atom becoming attached to the ortho and the para position thus producing a 1:1 ratio of either isomer.



Nitration of methylbenzene

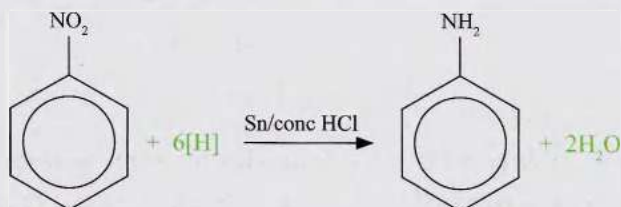
In the nitration of methylbenzene, the NO_2^+ cation is generated in situ by mixing concentrated sulphuric and concentrated nitric acid. The NO_2^+ ion is substituted on the ortho or para position producing a 1:1 ratio of each isomer at room temperature.



Since methylbenzene is more reactive than benzene, a lower temperature (30°C) is used to prevent more than one nitro group being substituted on the ring. At higher temperatures (50°C), two groups or three groups may be substituted on the ring.

Reduction of nitrobenzene

Nitrobenzene is reduced to phenylamine using a mixture of tin and concentrated hydrochloric acid. The mixture is heated under reflux for about half an hour.

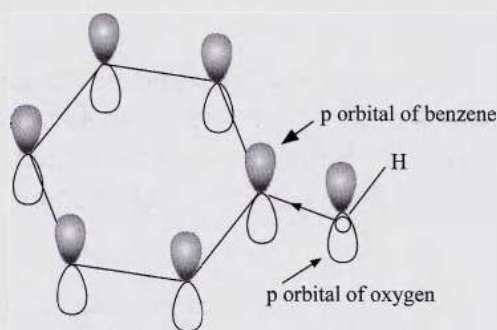


(NaOH liberates phenylamine from tin complex)

Sodium hydroxide solution is added to the product to liberate the phenylamine from the complexed tin ions.

Reaction of phenols

Phenol is a derivative of benzene in which one of the hydrogen atoms of the ring system has been replaced by a hydroxyl group. One of the lone pair of electrons in the p orbital of the O atom of the OH group of phenol overlaps with the p orbital of the benzene ring system.

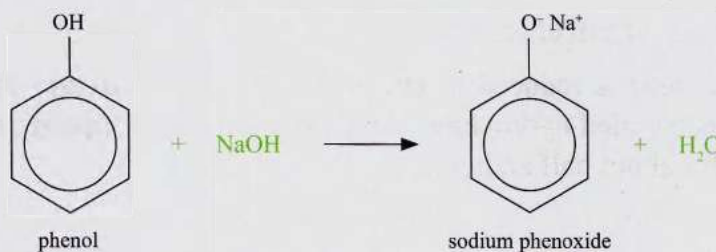


The interaction between the delocalized electrons in the benzene ring and the lone pair on the oxygen atom effects both the properties of the ring and the -OH group. The donation of the lone pair of the oxygen atom into the ring system increases the electron density around the ring. This activates the ring in phenol making it more reactive than benzene itself. Activation of the ring results in substitution reactions taking place at the 2,4 and 6 positions. It also causes the O - H to dissociate more easily therefore making it a weak acid.



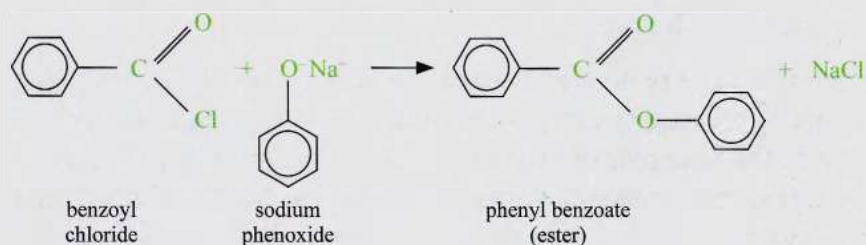
With NaOH

Since phenol is slightly acidic i.e. it has weak tendencies to lose the H^+ ion from the hydroxyl group, it dissolves readily in sodium hydroxide solution to produce a salt and water.



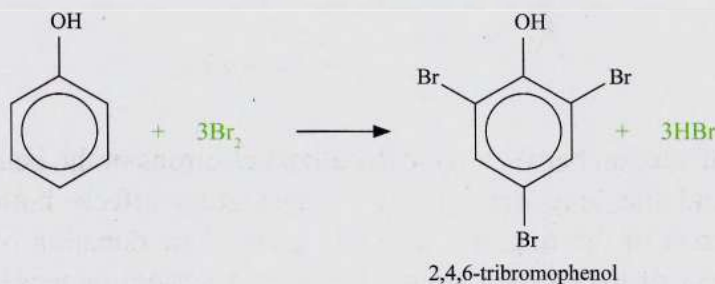
With acyl chlorides

Phenol reacts slowly with acyl chlorides at room temperature to form an aromatic ester and hydrogen chloride. To get a reasonably faster reaction with the acyl chloride, the phenol is first converted into sodium phenoxide by dissolving it in sodium hydroxide solution. The reaction of benzoyl chloride with sodium phenoxide to form phenyl benzoate and sodium chloride is given below.



With aqueous bromine

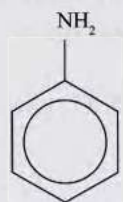
Phenol will react with aqueous bromine in the cold and in the absence of a catalyst to form 2,4,6-tribromophenol and hydrogen bromide. The aqueous bromine is decolourized and a white precipitate is formed which has an antiseptic smell.



In this reaction, tri-substitution occurs without the use of a Friedel-Crafts catalyst since the ring is highly activated and electrophilic substitution takes place with ease. This reaction can be used to distinguish phenol from other organic compounds.

Reactions of amines

Amines are derivatives of ammonia. They are classified as primary, secondary and tertiary amine depending on the number of R (alkyl or phenyl) groups attached to the nitrogen atom. Phenylamine is a compound in which one of the hydrogen atoms in an ammonia molecule has been replaced by a phenyl group.



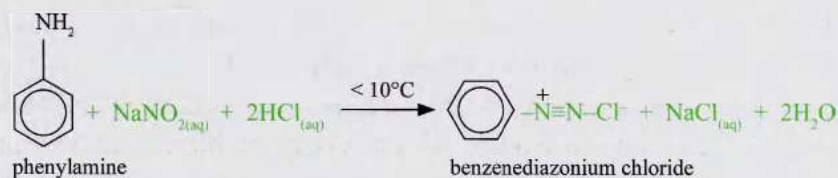
Phenylamine shows different properties from aliphatic amine because the lone pair on the nitrogen atom interacts with the delocalized electrons in the benzene ring. This makes the benzene ring in phenylamine more reactive than benzene itself. It also reduces the availability of the lone pair on the nitrogen to accept protons therefore making it less basic than aliphatic amines.

With nitrous acid

Nitrous acid (HNO_2) is unstable and is generated using a solution containing sodium nitrite with hydrochloric acid below 10°C .



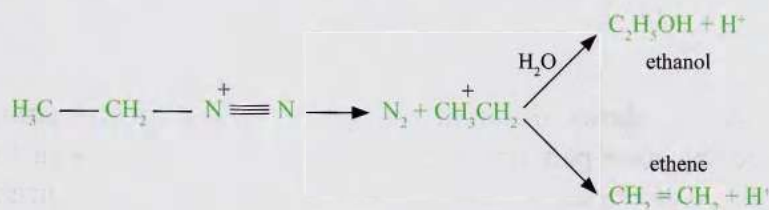
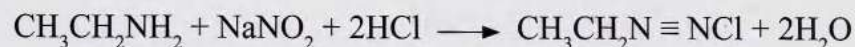
The hydrochloric acid reacts with the sodium nitrite to form nitrous acid and sodium chloride. Phenylamine reacts with the nitrous acid to form a diazonium salt.



The positive ion, containing the $\text{N} \equiv \text{N}^+$ group, is known as a diazonium ion. Diazonium salts are stable in solution below 10°C however they are unstable and explosive in the solid state. Above 10°C the solution of the salt decomposes to produce phenol and nitrogen gas is given off.



Aliphatic primary amines also react with nitrous acid to form diazonium salts however the diazonium salt is very unstable and decomposes to produce nitrogen gas and a carbocation. For example, when ethyl amine reacts with sodium nitrite and hydrochloric acid below 10°C, the ethyl diazonium ion is very unstable and rapidly decomposes to give off nitrogen gas and an ethyl carbocation. The carbocation further reacts to produce a mixture of ethanol, ethene and other products.



Azo compounds

The benzenediazonium ion is an electrophile. It will attack reactive nucleophilic sites in activated ring system such as phenol. The electrophile displaces the H^+ on the benzene ring of phenol in the para position forming a $\text{N}=\text{N}$ bond between the two aromatic rings. This is referred to as **azo-coupling**. For a faster reaction, phenol is dissolved in sodium hydroxide solution to give a solution of sodium phenoxide.



The product is a vivid orange colour and is used as dyes. Such dyes are called **azo-dyes**. They are usually stable compounds and have vivid colours such as red, orange, and yellow. The $\text{N}=\text{N}$ group is the structural feature which is responsible for the colour of azo compounds. It results in absorbance in the visible region of the spectrum and is called a **chromophore**.

The main uses of azo compounds are as dyes, food colourings and chemical indicators. More than half the dyes in commercial use are azo dyes. They are used to dye textile for clothing and decoration such as silk, leather, wool and cotton. Some azo compounds are used as acid-base indicators, due to their ability to show different colours in acids and alkalis e.g. methyl orange.



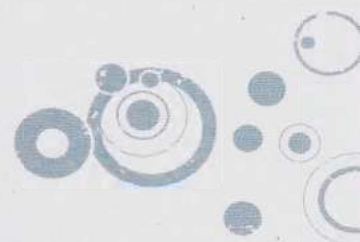
Azo compounds are used to dye clothing materials.





Questions

1. Distinguish between the following terms:
 - (a) Homolytic and heterolytic bond fission
 - (b) Electrophile and nucleophile
 - (c) Conjugative and inductive effect
2. (a) Write equations for the following reactions:
 - (i) combustion of octane
 - (ii) cracking of decane
 - (iii) chlorination of ethane(b) Describe the mechanism of the chlorination of methane.
3. (a) Describe the reaction of propene with the following:
 - (i) Bromine in tetrachloromethane
 - (ii) Hydrogen bromide
 - (iii) Acidified potassium manganate (VII)Write equations for the reactions (a) (i)-(iii) above.
(b) Describe the mechanism of the reaction of propene with hydrogen bromide.
4. Describe the reactions of propan-2-ol with the following:
 - (a) Acidified potassium dichromate
 - (b) Butanoic acid
 - (c) Alkaline iodine
5. Describe the mechanism for the hydrolysis of a named
 - (a) primary halogenoalkane
 - (b) tertiary halogenoalkane
6. Describe the reactions of propanal with the following:
 - (a) HCN
 - (b) 2,4-DNPH
 - (c) Alkaline diamminesilver (I) ions
 - (d) Alkaline copper (II) ions
 - (e) Alkaline iodine
 - (f) LiAlH_4



7. Describe the reactions of propanoic acid with the following:
- NaHCO_3
 - Mg
 - SOCl_2
8. (a) Carbonyl compounds are susceptible to attack by nucleophiles. Using ethanal and hydrogen cyanide explain the mechanism by which nucleophiles attack carbonyl compounds.
- (b) Other than nucleophiles, name two species that can initiate reactions in organic chemistry. Give an example of each species named.
9. (a) Name the type of reaction that occurs when ethene reacts with bromine in an organic solvent.
- (b) Describe the mechanism involved in this reaction.
10. Benzene reacts with a mixture of concentrated nitric acid and concentrated sulphuric acid to produce nitrobenzene.
- Write an equation to show the reaction between nitric acid and sulphuric acid.
 - Describe the reaction mechanism for the nitration of benzene.
 - Nitrobenzene is reduced by tin and concentrated hydrochloric acid to phenylamine. Write an equation for this reaction.
11. Benzene does not react with halogens on its own. However in the presence of a Friedel-Crafts catalyst, halogenation of benzene takes place at room temperature. Describe the mechanism for the halogenation of benzene with bromine in the presence of a Friedel-Crafts catalyst.
12. Methylbenzene commonly called toluene is a derivative of benzene in which one of the hydrogen atoms of the ring system has been replaced by a methyl group. Describe the reactions of methylbenzene with the following:
- Bromine in the presence of a Friedel-Crafts catalyst.
 - A mixture of concentrated nitric acid and concentrated sulphuric acid.

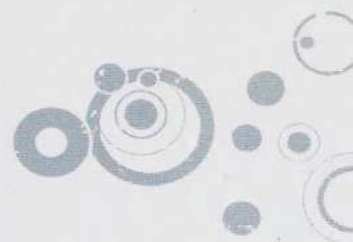
13. Phenol is a derivative of benzene in which one of the hydrogen atoms of the ring system has been replaced by a hydroxyl group. Describe the reactions of phenol with the following:

- (a) Aqueous bromine
- (b) Sodium hydroxide
- (c) Ethanoyl chloride

14. (a) Phenylamine and primary aliphatic amines react with the nitrous acid to form diazonium salts. Giving the conditions and relevant equations, illustrate the reaction of nitrous acid with

- (i) Phenylamine
- (ii) Ethyl amine

- (b) Compare the stability of the products formed in (i) and (ii) above.
- (c) Describe the reaction of the product formed in (a) (i) with phenol.
- (d) State the commercial significance of the reaction in (c) above.

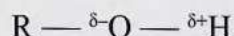




ACIDIC CHARACTER OF ALCOHOLS, PHENOLS AND CARBOXYLIC ACIDS

Acidity of alcohols

Alcohols are very weak acids with very large pK_a values. This originates from the fact that the oxygen atom of the O – H group pulls electron density away from the H atom. Charge dispersions therefore exist in the molecule as shown below.

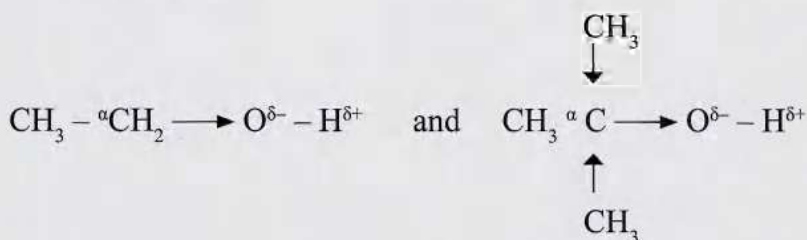


This loss of electrons allows H to become labile and the ionization can occur.



responsible for acidity

The shorter half arrow means it ionizes to a small extent. The pK_a of ethanol is 15.9 compared to water which is 15.73. The higher the pK_a value, the weaker is the acidic strength. Generally if the anion formed is stable then the compound tends to be acidic. If the anion is unstable then the alcohol is poorly acidic. Consider a primary alcohol versus a tertiary alcohol for example, ethanol versus 2-methylpropan-2-ol. Alkyl groups are electron donating and tend to push the electron density onto the α -C atom i.e the first carbon that attaches to the functional group. This in turn supplies electrons to the O atom. The polarity $O^{\delta-} - H^{\delta+}$ in alcohols is therefore lowered. The alcohols are less ready to lose a proton.



The oxygen atom has a great tendency to be protonated or rather to stay protonated. Thus alcohols are poor acids. Generally as the number of alkyl groups increase the acid strength decreases.



Acidity of phenols

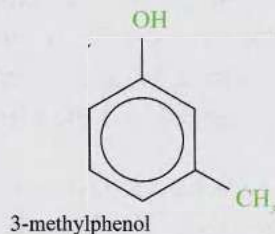
Phenol has the OH group attached directly to the benzene ring. Acidity is dependent on the stability of the phenoxide anion. In the phenoxide anion the negative charge is delocalized and becomes a part of the ring system. It is therefore a very weak acid since the electron on the O in the anion is unavailable to accept a proton. Phenol therefore readily gives up a proton in aqueous solution.



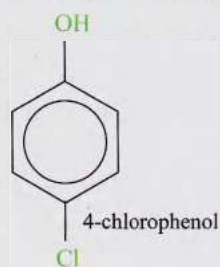
Phenol is not acidic enough to react with Na₂CO₃ to evolve CO_{2(g)}. Thus reaction with Na₂CO₃ can be used to distinguish phenol from carboxylic acids.

Substituents on the ring

- Electron releasing groups push the electron density into the ring which reduces the extent of delocalization of the lone pair of electrons on the O atom. The electron density on the O atom remains and it is available to accept a proton. Therefore the acidity of phenol with electron releasing groups is reduced. E.g. a CH₃ group on phenol.



- Electron withdrawing groups have the reverse effect in that they pull electrons away from the O making it more acidic. Therefore the H⁺ is lost easily and acidity increases. E.g. Cl, NO₂ or COOH group on phenol.

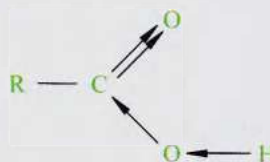


Acidity of carboxylic acids

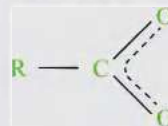
The acid strength depends on equilibrium.



Acidity depends on the readiness with which the O–H bond splits and the recombination of the anion with H_3O^+ . The movement of electrons in the carboxylic acid molecule is shown in the diagram below.



The H^+ is lost easily and the negative charge is delocalized in the available p orbitals of the carbon and oxygen atoms. The diagram below illustrates the structure of the carboxylate ion.



The carboxylate anion is therefore stable as the negative charge is equally shared by both the oxygen atoms. It is therefore a weak acid since the electron on the O in the anion is unavailable to accept a proton. A carboxylic acid is protonated less easily than the phenoxide ion of phenol and the alkoxide ion of an alcohol.

Chlorine is a highly electronegative element and tends to pull electron density towards itself. It pulls the delocalized electron density of the COO^- towards itself which enables the charge cloud to be spread throughout the anion more than in ethanoic acid. This further loss of electron density from the oxygen atom carrying the negative charge decreases its ability to accept a proton. As such chloro substituted ethanoic acids tend to give up hydrogen (H^+) easily and are therefore stronger acids. Tri-substituted acids are stronger than di-substituted acids which are stronger than mono substituted acids as demonstrated by the pK_a values shown in table 20.1.

Table 20.1
 pK_a values of
acids

Acids	pK_a
$\text{C}_2\text{H}_5\text{COOH}$	4.88
CH_3COOH	4.76
CH_2ClCOOH	2.86
CHCl_2COOH	1.29
CCl_3COOH	0.65



BASIC CHARACTER OF ALIPHATIC AMINES, AROMATIC AMINES AND AMIDES

Aliphatic amines

A base is defined as a proton acceptor. Amines are bases because they all contain a nitrogen atom containing a lone pair of electrons. This lone pair can easily form a dative bond with an H^+ ion in solution.



All amines do not have the same basic strength. The strength depends on the availability of the lone pair of electrons on the nitrogen atom to accept a proton. The more available these are the greater the basic strength. If we compare the basic strength of ammonia and methyl amine, a good indication is its K_b value. Generally the larger the K_b value or the smaller the pK_b value the stronger is the basic strength.

Methyl amine $pK_b = 3.34$

Ammonia $pK_b = 4.74$

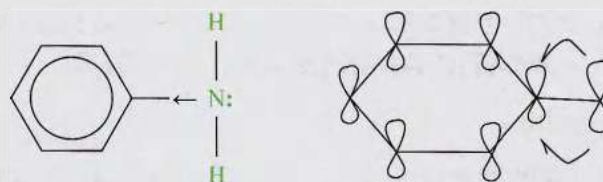
Hence methyl amine is a stronger base. Methyl amine contains an electron donating group which pushes electron density onto the nitrogen atom. This intensifies the negativity on the nitrogen atom making the lone pair of electrons more available to accept a proton.



Aromatic amines

Phenylamine has a K_b value of $4.2 \times 10^{-10} \text{ mol dm}^{-3}$. This implies that the lone pair of electrons on the nitrogen is not as available to act as a base as in methyl amine and ammonia. In phenylamine, the p orbitals of nitrogen carrying the lone pair of electrons are in close proximity to the p orbitals in the ring system. This allows overlap of the p orbitals to occur and the electrons become delocalized in the ring system.

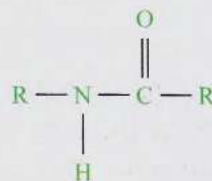




This delocalization means that the lone pair becomes part of the electron cloud of the ring system and is unavailable to accept a proton. Hence it is a much weaker base than methyl amine.

Amides

Amides have the general formula



In an amide, a pi bond is made by sideways overlap between p orbitals on the carbon and the oxygen. The lone pair on the nitrogen atom is almost parallel to these p orbitals, and overlaps with them as they form the pi bond. This is shown in Fig. 20.1 below.

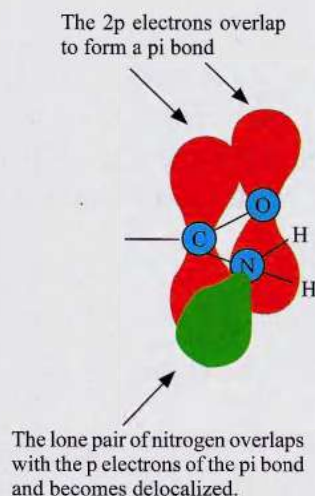


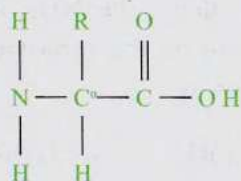
Fig. 20.1 Orbitals in amides

The lone pair of electrons of N is therefore unavailable to accept a proton as they are used in the delocalized electron cloud generating greater stability. Amides show little or no tendency to accept a proton and hence are very weak bases, almost neutral.



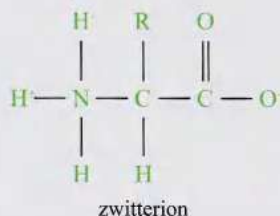
ACID-BASE PROPERTY OF AMINO ACIDS

Amino acids have the general formula as shown below.



The molecule has two functional groups attached to the α -carbon i.e. the first carbon that attaches to the functional group. This α -carbon is chiral except when R is the H atom as in the glycine molecule.

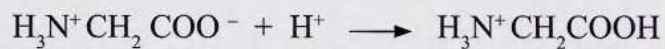
It is the variation in the R group that accounts for the twenty amino acids known. Scientists have discovered that amino acids can be recrystallized from aqueous solutions and these crystals had abnormally high melting points e.g. glycine (aminoethanoic acid) has a melting point of 234°C . This led scientist to believe that some form of ionic characteristics was present which was responsible for these large values even though it was a covalently bonded molecule. It was discovered that amino acids existed as dipolar ions in aqueous solution called **zwitterions**. This dipolar neutral ion resulted from the deprotonation of the COOH group and the simultaneous protonation of the NH_2 group.



The negative terminal of one amino acid is attracted the positive terminal of another amino acid generating electrostatic attractions. These attractions account for the high melting point of the crystalline amino acids.

Zwitterions can act as buffers in biological systems. They exhibit both the ability to donate protons and accept protons and are therefore amphoteric. If a bit of H^+ is added to an aqueous solution of amino acid, the pH will be unaffected. The zwitterion quickly accepts the H^+ protonating the COO^- group as shown in the following equation.



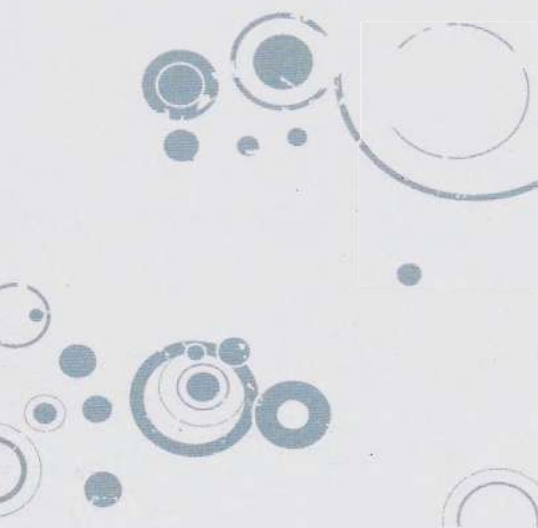


H^+ is removed thereby maintaining pH.

If a bit of OH^- ions are added, the NH_3^+ group quickly gives up an H^+ forming water ensuring the removal of the added OH^- as shown in the equation below.



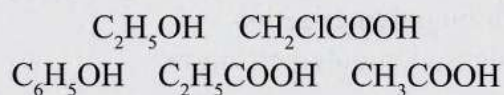
The OH^- is removed thereby maintaining the pH of the solution. Other amino acids behave similarly.





Questions

- Explain the acidic nature of the O – H bond in propanoic acid.
 - Place the following molecules in order of increasing acidic strength. Explain your answer.



- The pK_a values of ethanoic acid and chloroethanoic acid are 4.76 and 2.86 respectively.
 - State the meaning of the term pK_a and explain the significance of its value.
 - Account for the difference in pK_a values of ethanoic acid and chloroethanoic acid based on the structure of the molecules.
- With the aid of an equation explain the basic nature of ethyl amine.
 - The pK_b values of phenylamine and ethyl amine are 9.38 and 3.33 respectively.
 - What information does the pK_b value gives about the strength of a base?
 - Account for the difference in these pK_b values of phenylamine and ethyl amine.
 - Ethanamide and ethyl amine are aliphatic nitrogen compounds. Ethanamide is almost neutral and has a pK_a value of 15. Explain this difference in basic property between ethanamide and ethyl amine.
- Amino acids can be recrystallized from aqueous solutions. These crystals have high melting points.
 - Give the displayed formula of alanine ($\text{CH}_3\text{CHNH}_2\text{COOH}$).
 - Explain why alanine has a high melting point and is soluble in water.



In organic chemistry small molecules can join repeatedly to one another building up into a very large molecule called a **polymer**. These small molecules are rather reactive molecules called **monomers**. The two main types of polymerization processes are given below.

- Addition polymerization
- Condensation polymerization

Polymers can exist naturally or they may be synthetic (man-made). Natural polymers are those that exist in nature and include addition polymers such as rubber and condensation polymers such as proteins and carbohydrates. Synthetic polymers are quite common and also include addition polymers such as polyethene, poly vinyl chloride, and polytetrafluoroethene. There are also condensation polymers, which are synthetic in origin such as nylon 6.6 and terylene. This can be summarized in Fig. 21.1 below.

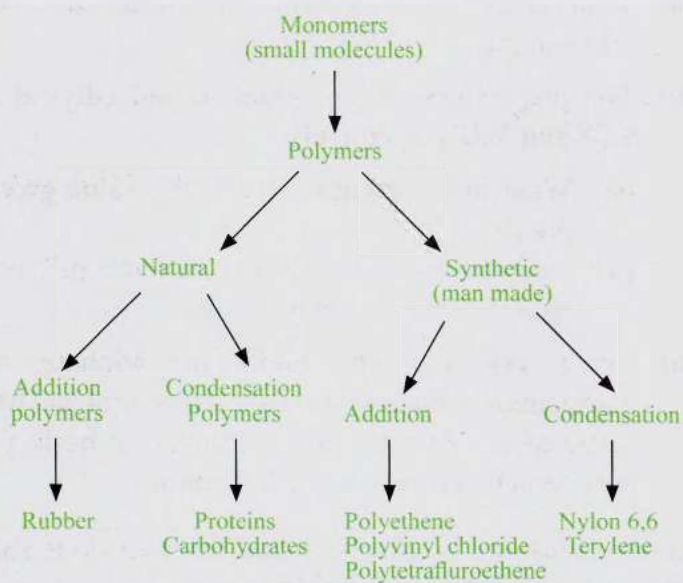


Fig. 21.1 Types of polymers.



ADDITION POLYMERIZATION

Addition polymerization involves the linking together of monomers with double or triple bonds. These unsaturated monomers have bonds which are able to break and link up with other monomers to form a repeating chain. Addition polymerization

is involved in the manufacture of polymers such as polyethene, poly vinyl chloride (PVC) and polytetrafluoroethene (PTFE).

Polyethene

In the polymerization of ethene, many molecules of the monomer add together to form a polymer.



The pi bond is broken to form a free radical. Free radicals are very reactive molecules which have unpaired electrons. The free radical mechanism can be divided into three stages. These are the initiation, the propagation and the termination stages.

The *initiation stage* is the formation of free radicals. The radicals can be formed from decomposition of organic peroxide molecules.



The free radical adds to an ethene monomer. It uses one electron from the pi bond to form a more stable bond with one carbon atom while the other electron forms a free radical on the other carbon atom.



The *propagation stage* is the rapid reaction of this free radical molecule with another ethene monomer to form longer chain free radical.

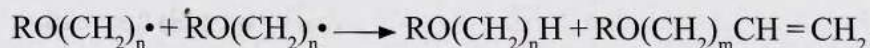


This free radical goes on to take part in another propagation reaction causing a chain reaction.

The *termination stage* occurs when two radicals react with each other.



A less common termination stage is disproportionation where two radicals meet and exchange a proton which gives two terminated chains. One chain is saturated and the other has a terminal double bond.



It should be noted that the monomer here is ethene and the polymer is named by placing the prefix 'poly' before the monomer giving the name polyethene. Polyethene may be of two types, low density or high density.

- **Low density polyethene** is produced at 200°C and a pressure of 15 atm with a trace of oxygen as a catalyst. It consists of branched molecules which does not pack tightly and gives a density of 0.91-0.94 g cm⁻³. It melts at about 105°C. It is durable, weather resistant and withstands attack by water, acids and alkali. It is used to make plastic bags, wraps for food and clothing items and electrical insulation.
- **High-density polyethene** makes use of a catalyst at 60°C and 1 atmosphere pressure. It consists of less branched molecules and is packed closely together to give a higher density (0.95-0.97 g cm⁻³). It melts at 135°C and has higher tensile strength. High-density polyethene is used to make tanks, crates, bottles and bowls.

Poly vinyl chloride (PVC)

Polychloroethene also called poly vinyl chloride (PVC) is one of the most widely used polymers in the world. PVC is produced by polymerization of the monomer chloroethene or vinyl chloride as shown in the equation below.



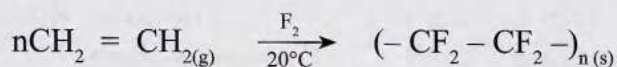
The chlorine atoms in PVC prevent it from burning readily resulting in fire resistant properties. PVC is also more rigid than polyethene as the chlorine atoms increase attraction between chains. However it can be made softer and more flexible by adding varying amounts of plasticizers (substances added to plastics to make them soft or pliable). This gives rise to a wide variety of uses for PVC. It is used in many aspects of construction, medical and household applications due to its durability, flexibility, sterilizability, cost effectiveness and flame resistant properties. Examples of uses include pipes, window frames, electrical conduits, floor coverings, blood bags, examination gloves, dialysis equipment and mouthpieces.

Polytetrafluoroethene (PTFE)

Polytetrafluoroethene (PTFE) is synthesized by the polymerization of tetrafluoroethene using high pressure.



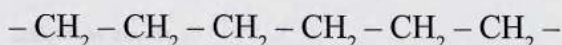
It can also be produced by the direct substitution of hydrogen atoms on polyethene with fluorine, using polyethene and fluorine gas at 20°C.



PTFE is a chemically inert plastic known by the trade names Teflon and Fluon. It is a stable heat-resistant material that exhibits anti-stick properties. It is used as heat-shields on spacecraft, as a non-stick coating on cooking utensils and as a lubricant. While PTFE itself is chemically inert and non-toxic, it begins to decompose above 300°C.

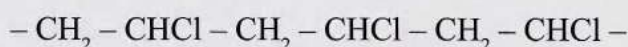
Repeat unit

The atoms that make up the backbone of a polymer chain have a regular order and this order repeats itself along the length of the polymer chain. The simplest structure or unit which is repeated in the polymer is called the **repeat unit**. It is put inside brackets, and the subscript *n* stands for the number of repeat units in the polymer chain. For example, part of the polymer chain in polyethene is



The chain is made up of a repeating $-\text{CH}_2$ group. Thus the repeat unit for polyethene is $(-\text{CH}_2 -)$.

For polychloroethene, part of the polymer chain is



The chain is made up of a repeating $-\text{CH}_2 - \text{CHCl}$ group. Thus the repeat unit for polychloroethene is $(-\text{CH}_2 - \text{CHCl} -)$. Similarly the repeat unit of polytetrafluoroethene is $(-\text{CF}_2 -)$.



CONDENSATION POLYMERIZATION

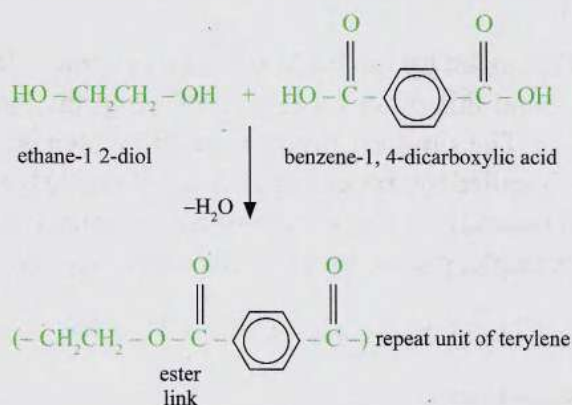
In condensation polymerization, a condensation reaction occurs in which monomers are joined together with the loss of small molecules such as water or hydrogen chloride. The product of condensation polymerization is dependent on the number of functional end groups of the monomer. Monomers with only one functional group end a growing chain. Those with two functional groups form linear polymers while those with more than two functional groups form three dimensional polymers with crosslinkages.



Condensation polymers are usually classified based on the linkage present in the polymer. For example, if ester linkages are present in the polymer, it is called polyester. Similarly, if amide linkages are present, it is called polyamide. Unlike addition polymers, condensation polymers are bio-degradable. The amide or ester bonds between monomers can be hydrolysed by dilute acid or bacterial enzymes breaking up the polymer chain.

Polyester

Polyester is produced in condensation reactions between diacids and dialcohols. They form ester linkages between monomers. **Terylene** is an example of a polyester. Also known by its trade name Dacron, it is made by polymerizing ethane-1, 2-diol (ethylene glycol) and benzene-1, 4-dicarboxylic acid (terephthalic acid).



Polyester is used to make clothing such as shirts, running shorts, track pants and windbreakers. It can also be made into curtains and draperies.

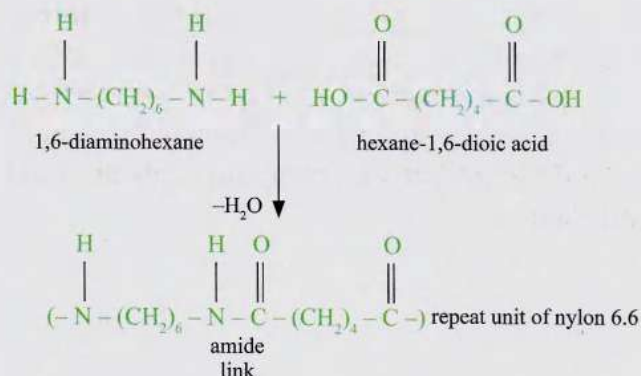


*Polyester is a condensation polymer that is used to make clothing.
PVC is an addition polymer used to make toys.*

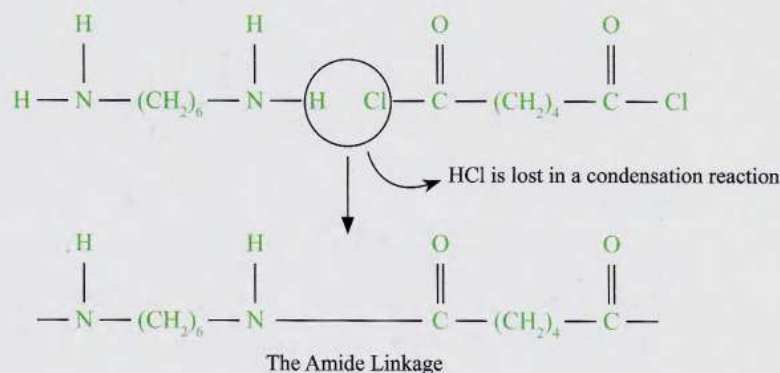
Polyamide

Polyamides can be manufactured from monomers such as diamines and di-carboxylic acid or di-acyl chlorides. A monomer with one amine and one carboxylic acid group on the same molecule can also be used. The carboxylic acids and amines link to form peptide bonds, also known as amide bonds.

Nylon 6.6 is a polyamide made from 1,6-diaminohexane and hexane-1,6-dioic acid. The units are joined to make the amide bonds as shown below.



In the laboratory, nylon 6.6 can be produced quite easily using acyl chloride functional groups instead of the acid groups. Acyl chlorides are much more reactive hence hexanedioyl chloride can be used instead of hexane-1,6-dioic acid.



The polymer is called nylon 6.6 because each repeat unit of the polymer chain has two stretches of six carbon atoms.

Nylon is very similar to the polyamides in silk and was an early substitute for silk. It is stronger, more durable and cheaper to produce than the natural fibres. Nylon is used to make a wide range of products such as nylon ropes, clothing, tufted carpets, parachutes and combat uniforms.



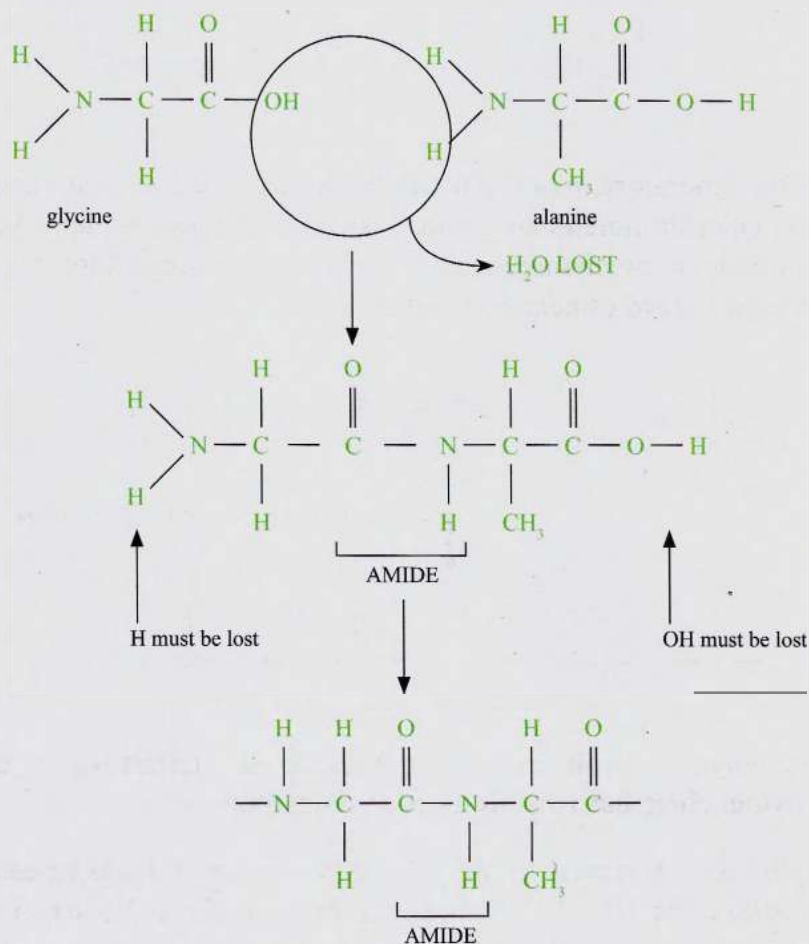


NATURAL POLYMERS

Proteins

Proteins are naturally occurring polyamides formed from the condensation of amino acids. Amino acids are difunctional molecules possessing a carboxylic acid group and an amine group attached to an alpha carbon atom. It is the acid group of one amino acid that condenses with the amine group of a second amino acid which results in the formation of an amide linkage.

When two amino acids are linked a **dipeptide** is formed. When many amino acids are linked a **polypeptide** is formed which further folds up into complex networks called the primary, secondary, tertiary and quaternary structures of protein molecules. In this example two different but simple amino acids are used namely glycine and alanine.



The primary protein structure is defined as the specific sequence of amino acids in the protein. The dipeptide consisting of two different amino acids, glycine and alanine could have two different

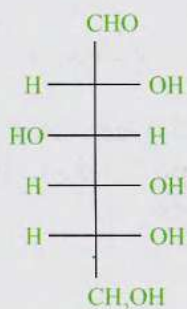


sequences i.e. gly - ala or ala - gly. In gly-ala, the glycine has the amine terminal end and alanine has the carboxylic acid terminal end. Different sequencing gives rise to different properties in proteins. Each protein has a different sequence of amino acids, the correct sequence being guided by the genetics of DNA and RNA.

Carbohydrates

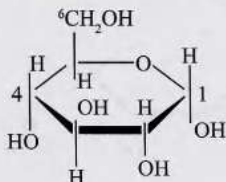
Carbohydrates are naturally occurring hydrated carbon compounds with the formula $C_x(H_2O)_y$. Carbohydrates include monosaccharides such as glucose and fructose, disaccharides such as maltose and sucrose and polysaccharides such as starch and cellulose. Glucose is a monomer unit that can undergo condensation reactions to form disaccharides and polysaccharides. Disaccharides and polysaccharides contain the ether linkage (C–O–C) which is also called the **glycosidic linkage**.

The structure of glucose is shown below. It contains five hydroxyl groups in addition to an aldehydes functional group. There are four chiral carbon atoms present in the open chain structure of glucose.



Open chain structure of glucose

Normally glucose exists in a ring structure as a result of intramolecular cyclization reactions. The ring structure results in another carbon atom becoming chiral i.e. the number 1 carbon atom has four different groups attached to it. This carbon atom is called an **anomeric carbon** and allows glucose to exist in two different forms. If the hydrogen on carbon atom 1 is above the plane of the ring, the alpha form of glucose exists. If the hydrogen is below the plane of the ring, the beta form of glucose exists.

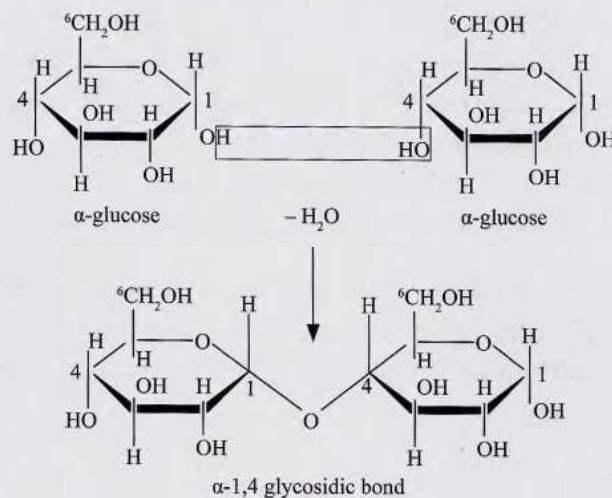


The α form of glucose

The glucose molecule can undergo condensation reactions with other glucose molecules to form di-, tri- and polysaccharides. Polymers formed from glucose include starch and cellulose.

Disaccharides

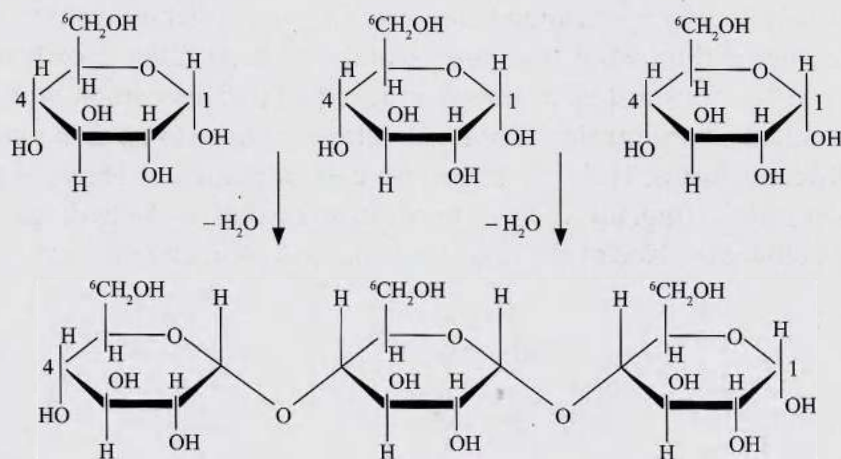
When a glycosidic bond is formed by the elimination of the H from the hydroxyl group on the number 1 carbon atom of a glucose molecule and the hydroxyl group on the number 4 carbon atom of another glucose molecule, an α -1,4 glycosidic linkage is formed.



A disaccharide is formed when two glucose molecules join together. Above shows how the disaccharide maltose is formed from two glucose molecules.

Tri-saccharides

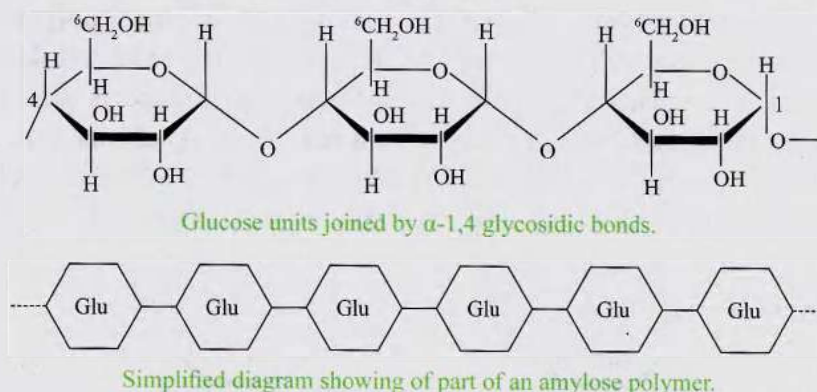
Tri-saccharides are formed when three monosaccharides join together. In this condensation reaction, two molecules of water are eliminated.



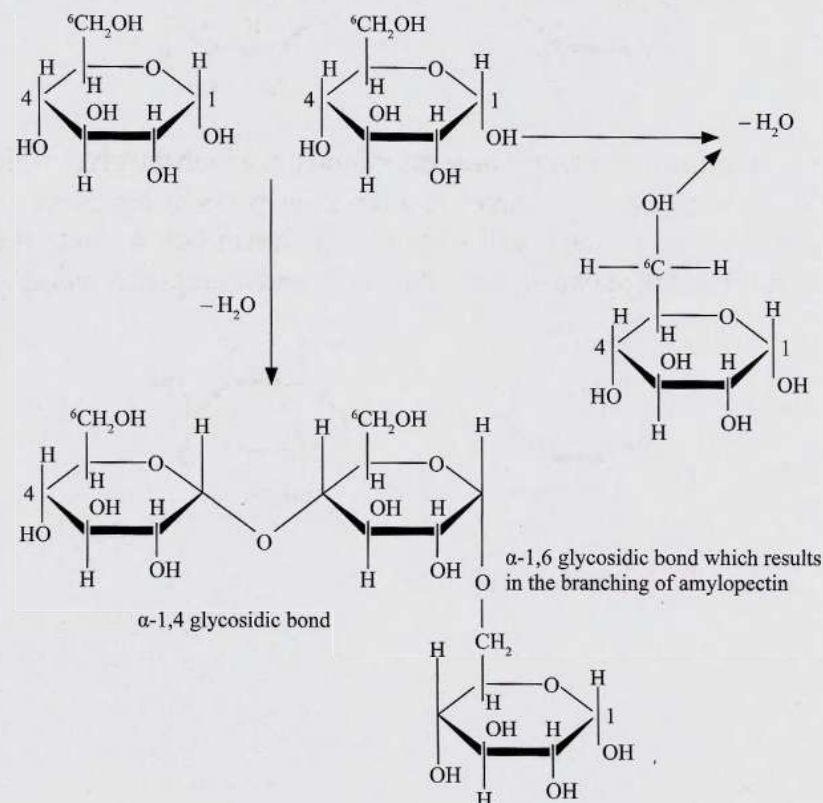
Tri-saccharides can undergo further condensation reactions with many glucose molecules to form polysaccharides.

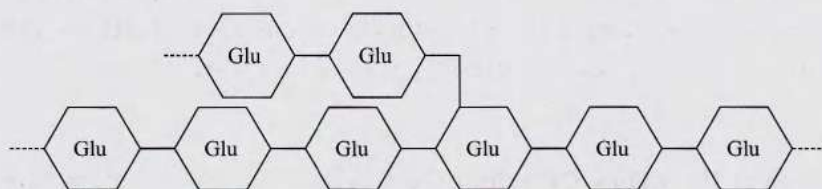
Starch

Starch is the major carbohydrate reserve in plant. It consists of two types of polymers, amylose and amylopectin (pectin). Both consist of glucose molecules which are linked by α -1,4 glycosidic bonds. **Amylose** consists of thousands of glucose units mainly of unbranched chains with α -1,4 glycosidic bonds. The diagram below shows part of an amylose polymer.



Amylopectin consists of glucose molecules which are linked by α -1,4 glycosidic bonds however about one in every twenty glucose unit is linked by an α -1,6 glycosidic bond forming branch-points. The diagram below shows part of an amylopectin polymer.

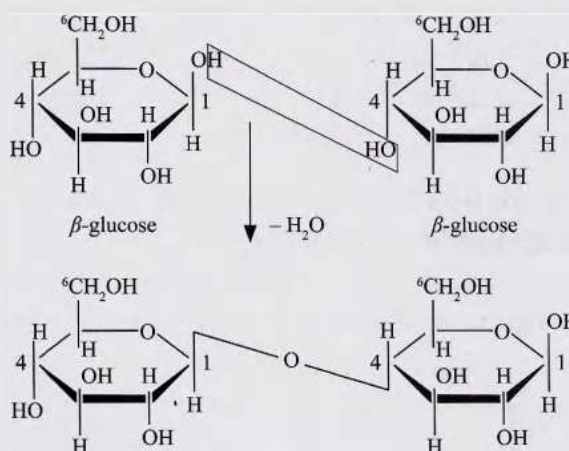




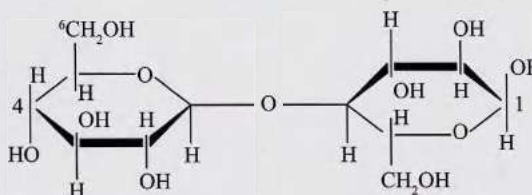
Simplified diagram showing of part of an amylopectin polymer.

Cellulose

Cellulose is another polymer of glucose but it is formed from β -glucose. It is a structural polysaccharide which gives rigidity and strength to plant cell walls. Cellulose is a highly complex polymer which is indigestible by humans because the enzyme cellulase which is responsible for the breakdown of cellulose is absent from our bodies but is present in animals such as rabbits, cows and other ruminant animals. Cellulose forms microfibrils which form macrofibrils which have tremendous tensile strength.



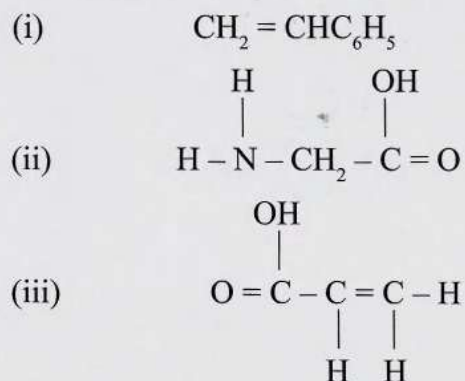
It is extremely important to note the manner in which the glycosidic linkage is represented. There are alternative ways of representing this glycosidic linkage, one of which is shown below. Note the orientation of the sugars in the molecule and its representation.



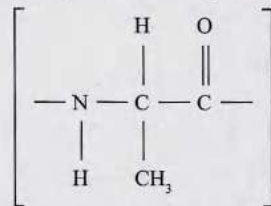


Questions

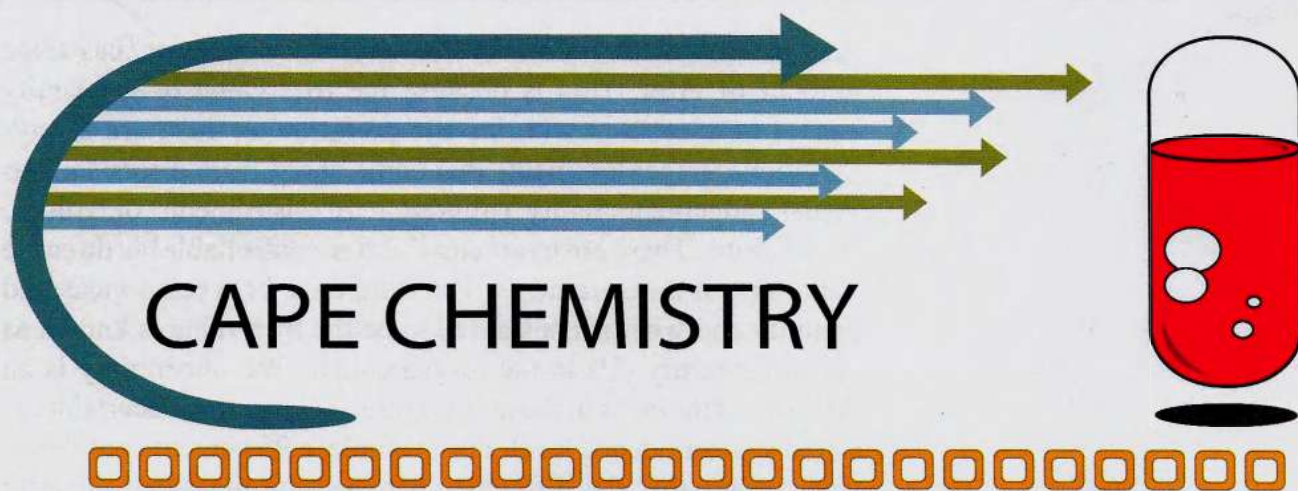
1. Differentiate between addition and condensation polymerization.
2. Polyester can be formed from the reaction of a dialcohol ($\text{HO} - \text{X} - \text{OH}$) and a diacid ($\text{HOOC} - \text{Y} - \text{COOH}$). Illustrate the formation of two repeat units of polyester using the diacid and dialcohol monomers.
3. Using three monomer units of $\text{CH}_2 = \text{CHCN}$, show part of the structure of the polymer formed from this monomer.
4. Glucose is the monomer unit for the naturally occurring polymers amylose and cellulose. Show how part of the structure of each polymer is formed from a glucose monomer.
5. Suggest with a reason the type of polymerization you would expect to occur in the following monomers:



6. (a) Name the type of polymerization involved in the formation of polychloroethene.
(b) Describe the mechanism for this type of polymerization.
(c) Name a synthetic polyamide and draw the repeat unit of the polymer named.
(d) The repeat unit of polymer X is given below.



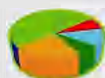
- (i) Name the type of polymerization involved in the formation of polymer X.
(ii) Draw the displayed formula of the monomer used in the formation of polymer X.

A graphic of a molecular model with four colored spheres (yellow, purple, light blue, and orange) connected by an orange ring.

SECTION 5

Analytical Methods and Separation Techniques

Any measurement, no matter how precise or accurate, has some amount of error. This is because the true value of a quantity cannot be measured with infinite precision as there are always variations in measurements that come about from errors such as visual judgement, faulty calibration of instruments or voltage fluctuations. These errors are small and uncontrollable but do cause variations in measurements. The difference between a measured quantity and what is considered to be the true value is known as the **uncertainty** (U) in the measurement. The uncertainty is an estimate of the error in the measurement. Generally, uncertainty is stated at a confidence level. For example, a 95 percent confidence level means that the difference between the measured quantity and the true value is expected to be within a specified range, $\pm U$, 95 out of 100 times.



ACCURACY AND PRECISION

Two concepts that deal with measurements are accuracy and precision. The **accuracy** of the measurement refers to how close the measured value is to the true or accepted value. **Precision** refers to the agreement between two or more measurements that have been carried out exactly the same way.

A dartboard analogy is often used to illustrate the difference between accuracy and precision. Imagine yourself throwing darts trying to hit the middle circle of the board. The closer the dart hits to the middle, the more accurate throws are. However if you miss the middle circle with every throw, but all of your darts land close together, your throws can still be very precise.

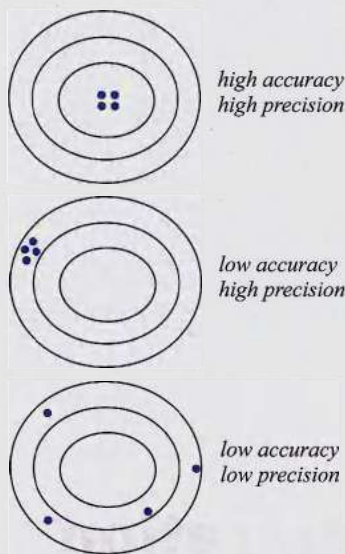


Fig. 22.1

Fig. 22.1

It must also be noted that precision has nothing to do with the true or accepted value of a measurement. Precision is determined with replicate measurements. **Replicate measurements** are obtained when a number of samples are analyzed in exactly the same way. Therefore, it is quite possible to be very precise and totally inaccurate.



Accuracy can be expressed in terms of either absolute or relative error. The **absolute error (E)** is found by subtracting the true or accepted value (x_t) from the measured value (x_m).

$$E = x_m - x_t$$

The value of the absolute error may be positive or negative. The **relative error (E_r)** is a measurement of the absolute error relative to the true or accepted value.

$$E_r = (x_m - x_t) / x_t$$

Relative error may be expressed in percent, parts per thousand or parts per million depending on its magnitude. Errors affecting experimental analysis are of two types. These are random or indeterminate errors and systematic or determinate errors.



RANDOM ERRORS

Random errors are the existing fluctuations of any measuring apparatus usually resulting from the experimenter's inability to take the same measurement in exactly the same way to get the exact value. Even the process itself may introduce variables that cause measurements to fluctuate. For example, to calibrate volumetric glassware, the mass and temperature of a liquid of known density contained in the glassware is measured. There are many sources of random errors associated in the calibration. These are small and uncontrollable variables such as

- visual judgment with respect to reading the marking on the glassware and the thermometer
- temperature fluctuations which affect the volume of the glassware, the viscosity of the liquid and the performance of the balance
- drafts that cause variation in the balance readings

Each error can cause a measurement to be high or low by a fixed amount, $\pm U$. Each error is too small to be eliminated but the accumulated effect of individual errors can cause replicate measurements (repeating the experiment in the same way) to fluctuate randomly. These small errors can occur in the same direction to produce a large positive or negative net error or they can occur in opposite direction to cancel out each other. Thus the average of several measurements is more reliable than any single measurement. The distribution of replicate measurements generally approaches that of a bell-shaped curve as shown in fig. 22.2.



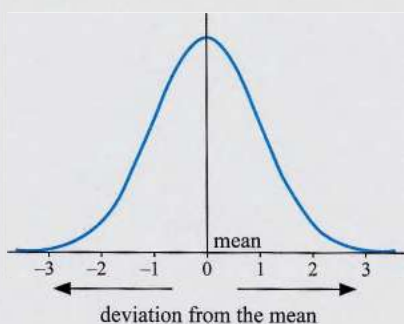


Fig. 22.2

It shows the symmetric distribution of measurements around a central value of a set of measurements. The **mean** or **average** is widely used as the central value for a set of measurements.

Fig. 22.2

Random errors affect the precision of a measurement. Precision is usually measured in terms of the deviation of a set of results from the mean value of the set. This is measured using the **standard deviation (s)**.

Average or mean value

The mean is calculated by dividing the sum of the replicate measurements by the number of measurements in the set. This is represented as

$$\bar{x} = \frac{\sum x_i}{N}$$

where x_i is the individual values of x making up the set of N replicate measurements and $\sum x_i$ is the sum of all the values of x_i for the replicates.

Example 1

Table 22.1

Below shows the results from five replicate samples in a titration.

Sample	Titre value / cm ³
1	20.10
2	20.05
3	19.80
4	20.25
5	19.95

Calculate the mean titre value from the data in Table 1.

$$\begin{aligned} \text{Mean} &= \bar{x} = \frac{20.10 + 20.05 + 19.80 + 20.25 + 19.95}{5} \\ &= 20.03 \text{ cm}^3 \end{aligned}$$

Standard deviation

The standard deviation (s) is a measure of the variation of a set of measurement about its mean value. It is typically called the uncertainty in a measurement. It tells how values bunch together from the mean in a set of data. When the values are tightly bunched together and the bell-shaped curve is steep, the standard deviation is small and the uncertainty in measurement is small. When the

values are spread apart and the bell curve is relatively flat, the standard deviation is relatively large and so to the uncertainty in measurement.

The standard deviation is calculated from the formula

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}}$$

Example 1

Calculate the standard deviation for the data shown in table 22.2

Table 22.2

x_i	Titre value	Deviation from mean $/ x_i - \bar{x} /$	$(x_i - \bar{x})^2$
x_1	20.10	0.07	0.0049
x_2	20.05	0.02	0.0004
x_3	19.80	0.23	0.0529
x_4	20.25	0.22	0.0484
x_5	19.95	0.08	0.0064
$\sum x_i$	100.15		$\sum (x_i - \bar{x})^2 =$ 0.113
Mean = $\frac{100.15}{5} = 20.03\text{cm}^3$			
Standard deviation = $\sqrt{\frac{0.113}{4}} = \sqrt{0.02825} = 0.168\text{ cm}^3$			



SYSTEMATIC ERRORS

A systematic error is a consistent difference between a measurement and its true value that is not due to random chance. It affects all the data in a set in the same way each time a measurement is made. There are three sources of systematic errors. These are

- **Instrument errors** – these are caused by errors such as faulty calibrations, instruments being used under different conditions from which they were calibrated or unstable power supply. These errors can be eliminated by calibration or checking the instrument against a standard.
- **Method errors** – these arise from behaviour of reagents and reaction such as incompleteness of reaction or occurrence of side reactions which interfere with the measuring process. These errors are difficult to detect and correct.
- **Personal errors** – these result from personal judgment



such as the colour of a solution at the end point in a titration or estimating measurements between two scale markings. These errors can be minimized by care and self discipline.

These errors affect the accuracy of a measurement. When the magnitude of the error is independent of the size of the sample being measured, the error is referred to as a **constant error**. This means that whether a small or large sample is used for analysis, the magnitude of the error is the same. Constant errors are minimized by using a large as possible sample. When errors vary with the size of the sample, they are referred to as **proportional errors**. This means that the magnitude of the error increases or decreases as the size of the sample increases or decreases.



ASSESSING DEGREE OF UNCERTAINTY IN MEASUREMENTS

Most common measurements recorded are volume, mass and temperature. Common pieces of laboratory apparatus used to measure volume are burette, pipette and volumetric flask. The top-loading balance and the analytical balance are used to measure mass while the thermometer is used to measure temperature. Uncertainty in measurements can be a result of the limitation of the measuring instrument (systematic error) and the skill of the experimenter making the measurements (random error).

Measuring volume

To avoid introducing systematic errors into volume measurements, burette, pipette and volumetric flask must be properly calibrated. Furthermore, to reduce the random errors the experimenter should develop the skills for making measurements. The quality of the measurements obtained from these apparatuses depends on the care taken in calibrating and in using each instrument.

To calibrate a 10 cm³ pipette

- Place distilled water in a beaker and let it stand for about 15 minutes then measure the temperature of the water.
- Using an analytical balance, weigh a clean dry conical flask with a stopper.
- Fill a 10 cm³ pipette with the water from the beaker and place the water into the conical flask. Stopper the flask.
- Weigh the conical flask and water and record the difference in weight.



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- Fill a 10 cm³ pipette with the water from the beaker and place the water into the conical flask. Stopper the flask.
- Weigh the conical flask and water and record the difference in weight.



- Repeat the above procedure three more times.
- Calculate the mean mass of the four pipette measurements.
- Determine the density of water at the temperature measured using the tabulated density of water.
- Then find the mean volume of water delivered by the pipette using the formula

$$\text{Volume} = \text{Mass} / \text{Density.}$$



MEASURING MASS

Increasingly, masses are measured using electronic balances.

Top-loading balances have a capacity of several hundred grams and are used to measure masses to $\pm 0.01\text{g}$. Analytical balances are limited to capacities of about 100g and are used to determine masses to $\pm 0.0001\text{g}$. Vibrations and air currents around the balance pan can result in fluctuation of measurements and affect the quality of the measurement. Measuring substances above or below room temperature on the balance pan can set up convection currents which can cause the measurement to fluctuate. These sources of error increase as the sensitivity of the balance increases.

It must also be remembered that although electronic balances have a tare or zero function, systematic errors can also arise from voltage fluctuation or faulty electronics. Thus it is common to weigh masses by difference in the laboratory.

Calibration is important to the accuracy of any balance. It is done by giving a zero point and establishing the maximum capacity weight. The balance can now accurately calculate all amounts in between zero and full capacity. Usually the calibration weight is purchased with the balance.

To calibrate an electronic balance

- Place the balance on a flat surface
- Turn on the balance and allow the unit to warm as specified in the manual
- Set the balance on calibration mode. The balance will display "CAL",
- Nothing should be on platform (this is calibrating the unit with nothing on the platform)

Temperature($^{\circ}\text{C}$)	Density (g/cm^3)
15	0.9991
16	0.9989
17	0.9988
18	0.9986
19	0.9984
20	0.9982
21	0.9980
22	0.9978
23	0.9975
24	0.9973
25	0.9970
26	0.9968
27	0.9965
28	0.9962
29	0.9959
30	0.9956

Table to show the density of water (g/cm^3) vs temperature ($^{\circ}\text{C}$)

Mass of KHSO_4 and weighing bottle /g	8.55
Mass of weighing bottle /g	6.30
Mass of KHSO_4 /g	$8.55 - 6.30$ $= 2.25$

Table to show weighing by difference of KHSO_4



- After a moment the balance will display the calibration mass needed, e.g. 200 g, at this time place the calibration mass 200 g on the balance pan.
- Press the enter button.
- The unit is now calibrated.



MEASURING TEMPERATURE

Liquid-in-glass thermometers are generally used in the laboratory to measure temperature. These should be calibrated regularly to ensure readings are correct. A properly calibrated thermometer can have an uncertainty in measurement of $+ 0.01^{\circ}\text{C}$ in the range of 0 to 100°C . Thermometers should not be used if there are cracks, internal condensation or liquid separation in them as these would give inaccurate measurements.

To calibrate a thermometer at 0°C

- Fill Styrofoam cup with crush deionised ice.
- Add cold deionised water to cover the ice.
- Place a calibrated thermometer into the ice-water mixture to make sure the mixture is 0°C .
- Insert the thermometer to be calibrated alongside the calibrated thermometer in the ice-water mixture and periodically stir for about 2 minutes for readings to stabilise.
- Take three readings for each thermometer within a 5 minutes span.
- Find the mean value for the readings of each thermometer and compare the values.
- If the mean is within $+ 0.5^{\circ}\text{C}$, correction to the thermometer measurement can be made using a calibration table for the thermometer.





CALIBRATION CURVE

A calibration curve establishes the relationship between the input and output of a measuring device. It is generally used to determine the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration. The standard samples of known concentration would be the input while the response of the measuring device such as absorbance would be the output. The measured output (y) can be plotted as a function of the input known values (x) to develop a calibration curve for the measuring instrument. For example, table 22.3 shows the absorbances for a set of known concentration of iron.

Table 22.3
Absorbance of Fe

[Fe] / ppm	Absorbance
0.0	0.0
2.0	0.15
4.0	0.31
6.0	0.45
8.0	0.59
10.0	0.75
Sample X	0.52

A plot of absorbance versus concentration approximates a straight line.

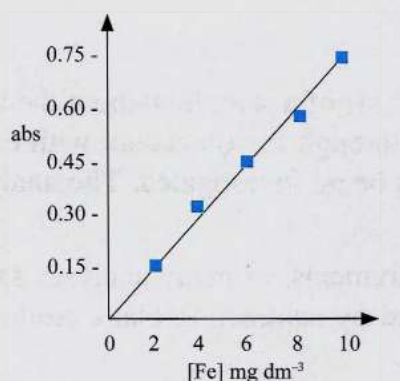


Fig. 22.3

Calibration curve showing
absorbance versus [Fe] / mg dm⁻³

Notice not all the points are exactly on the line because of uncertainties in the measuring process. Thus the best straight line is drawn through the points. The calibration curve can be used to



determine the concentration of an unknown iron sample X based on its absorbance. The unknown concentration of X would be the input while the absorbance value would be the output. If the absorbance value is 0.52 then the concentration of the unknown sample can be found by interpolation of the graph as shown in Fig. 22.4

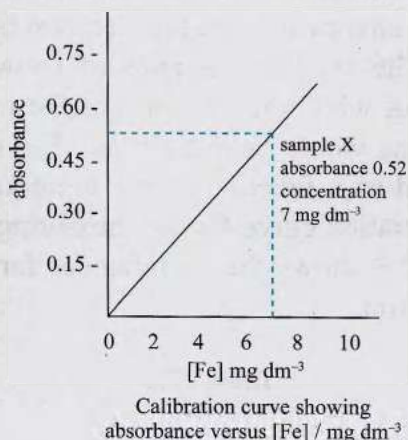


Fig. 22.4

Sensitivity

Sensitivity is the ability of a method to discriminate between small differences in measurements. In analytical measurements, sensitivity is often referred to as **calibration sensitivity** which is the change in the response signal per unit change in the analyte concentration. This means that the calibration sensitivity is the change in the output per unit change in the input of a measuring device which is the slope of the calibration curve. Therefore for the straight line, $y = mx + c$, the sensitivity is m . A method which produces a steeper calibration curve indicates that it is more sensitive.

Blanks

A blank is an analysis of a sample without the analyte, that is, a sample that goes through the procedure with everything except the species that is being investigated. The analysis of blanks is very important to

- zero instruments, in many analyses sample results are calculated by subtracting blank readings from sample readings.
- monitor quality control of reagents and check for contaminants.
- estimate detection limits.

Generally blank analyses are not zero because of interferences (see below). However for convenience, some analysts use it to

adjust the instrument to zero. This is equivalent to subtracting the blank value from the values of the standards before plotting the calibration curve. Usually a minimum of ten blanks is analyzed and the mean and standard deviation of the blanks are used to assess interference and to determine the detection limit.

Detection limit

The **detection limit** identifies the lowest concentration of an analyte that can be detected at a known confidence level. Detection limit is usually expressed in the concentration unit parts per million (ppm). Analysts use the term detection limit to express sensitivity. For example, a technique that has detection limit of 0.01 ppm is 100 times more sensitive than a technique with a detection limit of 1.0 ppm. Detection limit is related to sensitivity by the expression

$$DL = \frac{ks_b}{m}$$

Where s_b is the standard deviation of the blank, m is the calibration sensitivity and k is a factor chosen to be 2 or 3 depending on the confidence level.

Interferences

Interferences are caused by substances that prevent the direct measurement of an analyte. For example, electrical measurements are made in areas where there are electric and magnetic fields. These fields usually produce noise which gives a background signal that interferes with the electrical signal in measurements. Noise limits the sensitivity of the instrument. Blanks are used to check the instrument performance and the assessment of noise is determined from the standard deviation of a set of blanks.

Spectral interferences are encountered in atomic absorption spectroscopy. This occurs when particulate matter from the atomization process scatters incident radiation or when the absorption of interfering species is close enough to the analyte wavelength that overlapping of spectral lines occur.

Interferences may also be caused by contaminants in solvents, reagents or glassware. The use of high purity reagents and solvents and scrupulous cleaning of equipment is necessary to help minimize interferences.





Questions

1. Distinguish between the following:
 - (a) Random error and systemic error
 - (b) Accuracy and precision
 - (c) Absolute error and relative error
2. A technician analyzes samples of a compound XO for the mass constituent X. The mass of X present in each sample is given below.

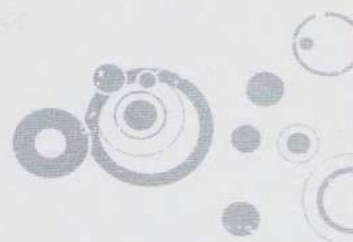
Sample	Mass of X/g
1	20.55
2	21.05
3	20.50
4	20.75
5	20.47
6	20.93
7	20.66
8	20.54

- (a) Calculate the mean and standard deviation of the values obtained.
 - (b) What does the standard deviation value indicate about the measurements?
3. An analyst investigating the concentration of iron in four samples of soil A, B, C and D by atomic absorption prepares five standard solutions which give the following absorbances.

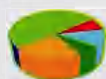
Solutions	Iron concentration/ppm	Absorbance
1	0.20	0.042
2	0.40	0.085
3	0.80	0.170
4	1.20	0.255
5	1.60	0.340



- (a) Plot the calibration curve of absorbance on the y-axis against iron concentration on the x-axis.
- (b) Given that the absorbances of samples A, B, C and D are 0.50, 0.65, 0.180 and 0.80 respectively, determine the iron concentration in each of the four samples of soil.
- (c) Calculate the mean and standard deviation for the four samples of soil with respect to the iron concentration.



Spectroscopy is based on the interaction of electromagnetic radiation with matter. When electromagnetic radiation interacts with matter, it can be absorbed, emitted, reflected or scattered from the solid, liquid, or gas. This technique utilizes the fact that atoms and molecules have discrete energy levels (their energy levels are **quantised**) and transitions can only occur between them when an atom or a molecule absorbs or emits a quantum of energy that is exactly equal to the difference between two energy levels. Spectroscopy also extends to include techniques which do not involve electromagnetic radiation such as mass, acoustic, and electron spectroscopy.



ELECTROMAGNETIC RADIATION

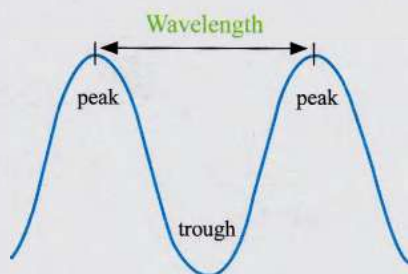


Fig. 23.1

Electromagnetic radiation can be viewed as a stream of photons which are particles with no mass travelling in a wave-like pattern at high velocities. The number of waves produced in one second is called the **frequency** and is measured in hertz (Hz). The distance between one wave peak and the next is called a **wavelength** and is measured in metres (m). Wavelengths can be very small e.g. 10^{-12} m or as large as many kilometres.

Fig. 23.1

Electromagnetic radiation is measured as a function of frequency and wavelength. All electromagnetic radiation travels at the speed of light in a vacuum (empty space). Thus the frequency and wavelength of electromagnetic radiation is related by

$$c = \nu \lambda \quad \text{..... equation (1)}$$

where c is the speed of electromagnetic radiation in a vacuum which is the speed of light ($3 \times 10^8 \text{ ms}^{-1}$), ν is the frequency and λ is the wavelength.

Using Planck's equation which shows that the energy of the photon is directly proportional to the frequency of the radiation

$$E = h\nu \quad \text{..... equation (2)}$$



where E is the energy, ν is the frequency and h is the Planck's constant (6.63×10^{-34} J sec), we can substitute $\nu = c / \lambda$ from equation (1) into equation (2) and so express a quantum of energy by the equation

$$E = hc/\lambda$$

Thus the energy of the photon is directly proportional to the frequency and inversely proportional to the wavelength, meaning that shorter wavelengths of radiation possess a greater quantum of energy.

A quantum of energy absorbed or emitted by an atom corresponds to electromagnetic radiation of a specific frequency or wavelength on the **electromagnetic spectrum**.

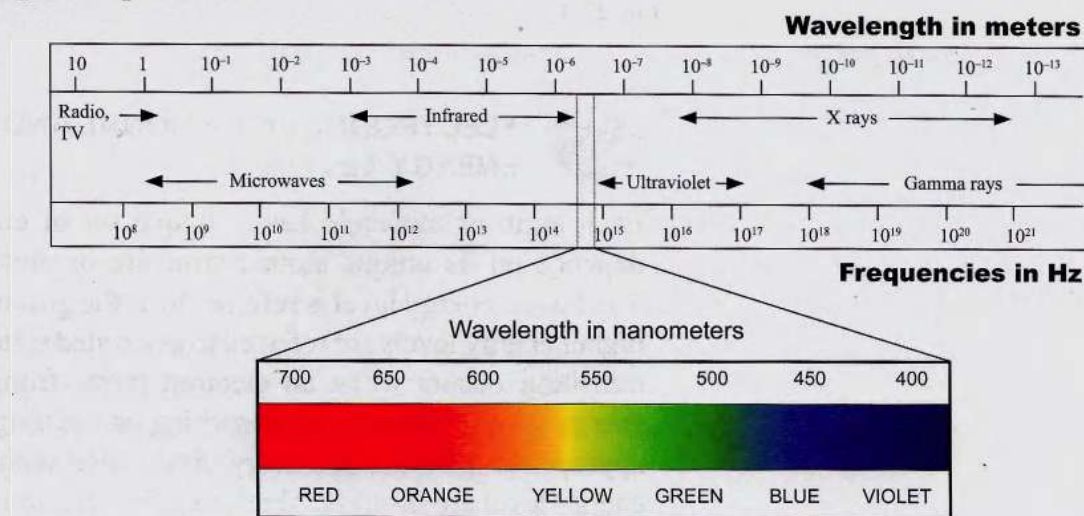


Fig. 23.2

The frequencies and wavelengths of some electromagnetic radiation



EXPOSURE TO ELECTROMAGNETIC RADIATION

Electromagnetic radiation is used on a daily basis as radio-waves in televisions and cell phones, microwaves in satellites and microwave ovens, infrared in toaster ovens and night-vision, and X-rays in medical imaging. However there is no question that exposure to high energy wavelengths are dangerous to humans. X-rays have great penetrating power and can damage living tissue resulting in birth defects and cancer. Although a small dose of ultraviolet radiation is beneficial to humans, larger doses can cause skin cancer and damage the retina of the eye.

Exposure to very high levels of low energy radiation can also be harmful due to the ability of radio frequency energy to heat



biological tissue rapidly. This is the principle by which microwave ovens cook food. As to low levels of exposure to radio frequency energy such as that used in cell phones, scientists are not yet certain what specific health effects may result from exposure over prolonged periods of time.

Visible light is a portion of the electromagnetic spectrum with wavelengths between 400 to 700 nanometers. It is this part of the electromagnetic spectrum that we see. Visible light have great use in the identification of different objects by their visible colours.

Visible spectrum							
Visible light	red	orange	yellow	green	blue	indigo	violet
Wavelength / nm	740-625	625-590	590-565	565-520	520-500	500-430	430-380

Fig. 23.3

The approximate wavelength interval for the spectrum of visible light.



ELECTRONIC, VIBRATIONAL AND ROTATIONAL ENERGY LEVELS

Each atom or molecule has a unique set of energy levels that depends on its unique atomic structure or molecular structure. The lowest energy level is referred to as the ground state while the higher energy levels are referred to as excited states. An electronic transition occurs when an electron move from one electronic energy level to another by absorbing or emitting radiation of an appropriate quantum of energy. Associated with each electronic energy level are discrete vibrational and rotational energy levels. The absorption or emission of energy in these energy levels results in vibration and rotation of molecules (not atoms). Atoms within a molecule can vibrate and also rotation about an axis through the center of gravity of the molecule can occur.

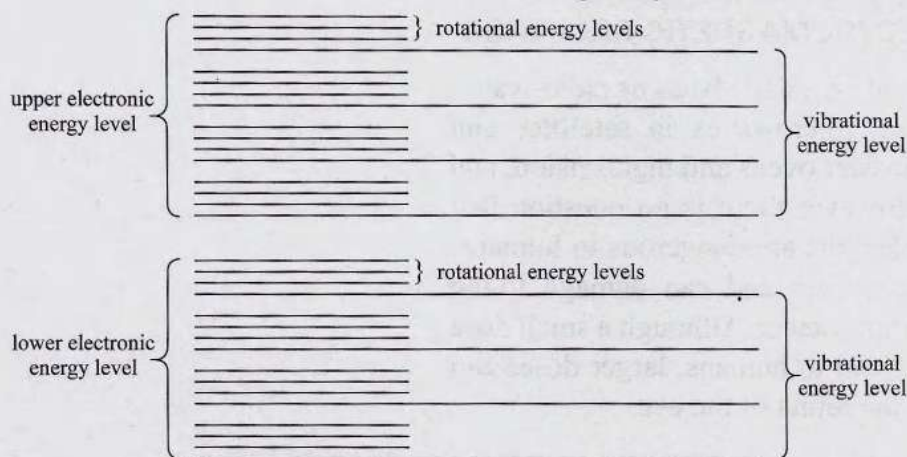


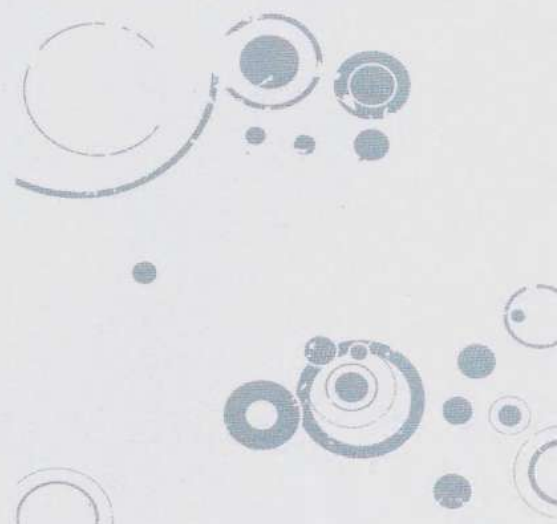
Fig. 23.4

Discrete energy levels superimposed on the electronic energy level.



The energy difference between *electronic* energy levels is greater than between the vibrational energy levels, which is greater than between rotational energy levels. Thus a larger quantum of energy is needed to cause transitions between electronic levels than between vibrational or rotational levels.

Spectroscopic methods of analysis depend on the different type of transitions which corresponds to different regions of the electromagnetic spectrum. Electronic transitions occur in the UV-visible region of the electromagnetic spectrum. Therefore UV-visible and atomic spectroscopic techniques are used to measure these transitions. Vibrational and rotational transitions occur in the infrared region and infrared spectroscopy is used to measure these transitions. A closer look at these techniques will allow an understanding of the various spectroscopic methods of analysis.



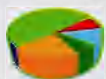


Questions

1.
 - (a) State the relationship between the energy, frequency and wavelength of a wave.
 - (b) Compound X absorbs light of frequency 156.8 MHz. Calculate the wavelength of the light absorbed.
 - (c) Calculate the frequency of the radiation of wavelength 200 nm.
2.
 - (a) Differentiate between electronic, vibrational and rotational energy levels.
 - (b) Explain what is meant by energy levels in atoms and molecules are quantised.
3. What energy is associated with the following transitions:
 - (a) 928 MHz
 - (b) 740 nm
 - (c) 2×10^8 HzIdentify the part of the electromagnetic spectrum where transitions (a)-(c) occur.
4. State the approximate wavelength ranges of the following:
 - (a) X rays
 - (b) Infrared radiation
 - (c) Radiofrequencies



Atomic spectroscopy is mainly used for analysis of metals in air, water and solid samples. It can be used to identify and measure the concentration of atoms in a sample regardless of how the atoms are combined. The outer electrons of atoms or ions exist in the ground state. When energy is supplied to these atoms or ions, the outer electrons absorb energy and are promoted to short-lived excited states. The excited electrons then emit energy and fall back to its ground state. This is referred to as relaxation. Since energy levels are quantised, an exact quantum of energy is required for electronic transition. This results in specific wavelengths being absorbed or emitted which produces a spectrum. These wavelengths usually correspond to ultraviolet and visible light. The spectrum formed by an element has a unique set of spectral lines which can be used to identify the element. The relative intensities of the spectral lines can be compared to a standard to determine the concentration of the element.



ATOMIC ABSORPTION SPECTROSCOPY (AAS)

If light is passed through the vapour of an element, certain wavelengths which are energetic enough to cause electronic transitions will be absorbed by the atoms and removed from the radiation. The absorption of energy by an element corresponds to specific wavelengths and appears as dark lines in the **absorption spectrum**. The amount of absorption depends on the number of atoms present which allows the concentration of the element in the sample to be determined.

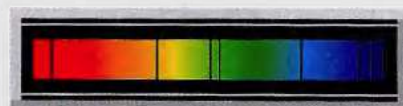


Fig. 24.1

A typical absorption spectrum

Fig. 24.1

Analyzing a sample by AAS

A sample for investigation by atomic absorption analysis is introduced into the atomic absorption spectrophotometer as aqueous ions. The solution is pulled into a nebulizer which mixes it with an oxidant (e.g. air or nitrous oxide) and a gaseous fuel (e.g. ethyne) to convert it into a fine mist. The mist is suctioned into the atomizer which is a low temperature flame which sits in the path of a light source. It converts ions and molecules into



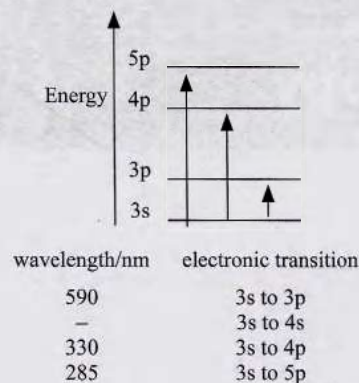


Fig. 24.2

The transitions of the outer electron of gaseous sodium atoms

gaseous atoms in the ground state before it interacts with the light source. A low temperature flame is used to minimize promotion of electrons so that gaseous atoms remain in the ground state.

As the sample is ignited in the flame, the solvent evaporates and gaseous atoms are excited by the light passing through the flame. The amount of light absorbed is proportional to the number of atoms in the ground state in the flame. The light is usually a hollow cathode lamp of the element that is being measured. For example a sodium lamp is used to measure sodium concentration. In this way the light source produces the exact wavelength for electronic transition.

Fig. 24.2

The wavelengths corresponds to transitions in atomic sodium in which the valence electron transitions from a 3s to 3p, a 3s to 4p and a 3s to 5p electronic state.

The light then passes through a monochromator and is resolved into spectral lines. The monochromator filters out unwanted light and isolates the absorption lines from light due to interference. The lines are detected and a computerized system converts the light intensity into absorbance and gives a readout. See fig. 24.3.

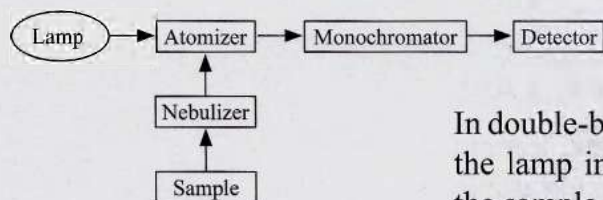


Fig. 24.3

Layout of an atomic absorption spectrophotometer

In double-beam instruments, a beam splitter divides the light from the lamp into two equivalent beams. One beam passes through the sample while the other beam passes through a reference cell. The detector compares the intensities of the sample and reference beams. This is shown in fig. 24.4.

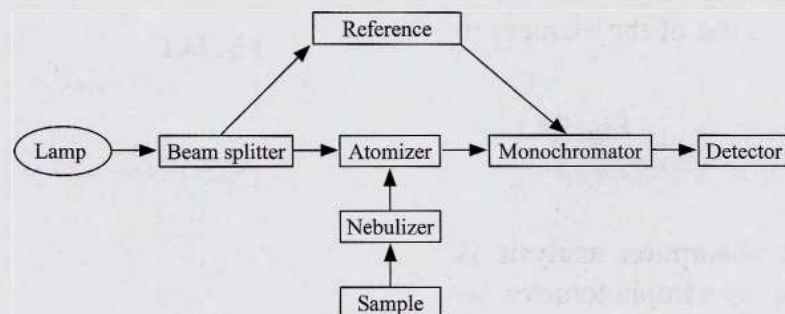


Fig. 24.4

Layout of a double beam atomic absorption spectrophotometer

Fig. 24.4



Atomic absorption spectrometer



ATOMIC EMISSION SPECTROSCOPY (AES)

Earlier we saw that evidence for the arrangement of electrons in the atom comes from emission spectrum of hydrogen. When atoms are supplied with heat or electrical energy to high enough temperatures, an electron in the ground state absorbs a quantum of energy and moves to an orbit with a higher energy level which is further away from the nucleus. This excited electron in the higher energy level cannot maintain this position for a long time and it falls back to a lower energy level. As it falls back it emits a quantum of energy which is equivalent to the difference in the energy levels. The emission of energy by an element corresponds to specific wavelengths on the electromagnetic spectrum and produces a unique **emission spectrum**. An emission spectrum shows coloured lines on a dark background.

► Fig. 24.5



Fig. 24.5

A typical emission spectrum

Analyzing a sample by emission spectroscopy is similar to that of absorption spectroscopic analysis. However a high-temperature energy source is used in the atomizer which provides sufficient energy to promote the atoms into high energy levels. Therefore the hollow cathode lamp and the beam splitter are not necessary in emission instruments. Since all atoms in a sample are excited at the same time, they can be detected simultaneously. This is an advantage of atomic emission spectroscopy compared to atomic absorption spectroscopy

Applications of atomic spectroscopy

Atomic absorption spectroscopy is an analytical method for determining the presence of metallic contaminants in both trace and major concentrations. More than half of the elements in the periodic table can be analyzed quantitatively in the range of parts per million. This method is sensitive and reliable for routine measurements such as quality control of metals in drinking water, factory effluents and foodstuff. It is also used in clinical diagnosis for example, to determine the concentration of Na^+ and K^+ ions in blood serum.

Standards and calibration curves

Variation in absorbance for a sample in two different spectrophotometers is possible due to the difference in sensitivity of the instruments. Therefore each time a spectrophotometer is used it is calibrated using a set of standards and a blank reference. Standards can be prepared by dissolving an accurate mass of



dry, high purity solid in deionized water and making it up to an accurate volume. For example, if 0.259 g of dry, high purity potassium nitrate is dissolved in 1 dm³ of water, then

$$[\text{KNO}_3] = \frac{0.259}{101} = 2.56 \times 10^{-3} \text{ mol dm}^{-3}$$

For low concentrations, mol dm⁻³ is not convenient instead individual ions are expressed in mg dm⁻³. Thus

$$\begin{aligned} [\text{K}^+] &= \frac{2.56 \times 10^{-3} \text{ mol}}{\text{dm}^3} \times \frac{39 \text{ g}}{\text{mol}} \\ &= 0.10 \text{ g dm}^{-3} \\ &= 100 \text{ mg dm}^{-3} \end{aligned}$$

Percentage and parts per million (ppm) can also be used as convenient units of concentration. Usually ppm is used for solids however it is sometimes used in aqueous solution since water and dilute solutions have a density of $\frac{1.00 \text{ g}}{\text{cm}^3}$.

ppm is 1 part in 1 000 000 i.e. $\frac{1 \text{ mg}}{1 \text{ kg}} = \frac{1}{10^6}$

1 kg has a volume of 1 dm³ so for aqueous solutions $\text{ppm} = \frac{\text{mg}}{\text{dm}^3}$.

The 100 mg dm⁻³ solution is referred to as the primary stock and can be diluted accurately to get other standard solutions. Having prepared a series of standards, a **blank** (0 ppm) is used as a reference to zero the spectrophotometer. A blank is a sample that contains everything but the absorbing species. Since there is no absorbing species present in the blank sample, the absorbance of the light passing through the blank is set to at zero. The absorbance of each solution and the unknown sample is then measured. The absorbance is plotted as a function of the known concentration of the series of standards to generate a calibration curve. The concentration of the unknown sample can be found by interpolation of the graph.

Example 1

An unknown sample X contains a trace of iron impurity. Determine the concentration of iron in sample X.

Accurately make up standards of 0.0, 2.0, 4.0, 6.0, 8.0 and 10.0 ppm Fe and measure the absorbance of each solution and unknown sample X at 248 nm. Plot a calibration curve from the set of data shown in table 24.1

Table 24.1
Absorbance of Fe

[Fe] /ppm	Absorbance
0.0	0.0
2.0	0.15
4.0	0.31
6.0	0.45
8.0	0.59
10.0	0.75
Sample X	0.52

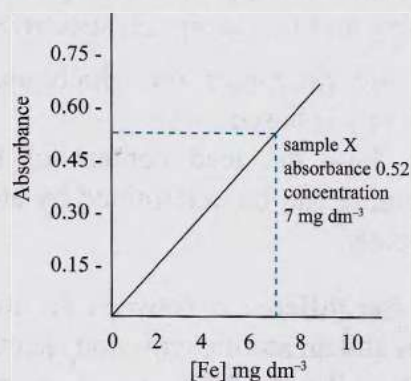


Fig. 24.6 Calibration curve showing absorbance versus $[\text{Fe}] / \text{mg dm}^{-3}$

The concentration of sample X is obtained from interpolation of the graph. An absorbance of 0.52 corresponds to a concentration of 7 mg dm^{-3} of iron as shown in fig. 24.6.





Questions

1.
 - (a) Explain the origin of atomic absorption spectroscopy.
 - (b) Discuss the importance of atomic absorption spectroscopy in analytical analysis.
2. The concentration of lead in a sample of blood can be determined using atomic absorption spectroscopy.
 - (a) Explain the principles on which atomic absorption spectroscopy is based.
 - (b) Describe how the lead content of the serum of a blood sample can be determined by atomic absorption spectroscopy.
3.
 - (a) Explain the difference between an atomic absorption spectrum and an atomic emission spectrum.
 - (b) Briefly describe the differences in principles on which atomic absorption spectroscopy and atomic emission spectroscopy operate.





ORIGIN OF ABSORPTION

Molecular absorption of ultraviolet and visible wavelengths usually forms one or more electronic absorption bands, each of which consists of closely spaced discrete lines. Each line results from the transition of an electron from the ground state to one of the many vibrational and rotational energy levels associated with each excited electronic energy level. The wavelength at which the sample shows maximum absorption is denoted by $\lambda_{\max}$, this is the tallest part of the peak for an absorption band.

► Fig. 25.1

Organic functional groups can be identified by their typical $\lambda_{\max}$ values while the concentration of a solution can be determined from the amount of light absorbed by a solution. The amount of light absorbed depends on the colour intensity of the solution which is directly related to its concentration. For example, a bright red solution has a higher concentration of a particular molecule as compared to a light red solution of the same molecule.

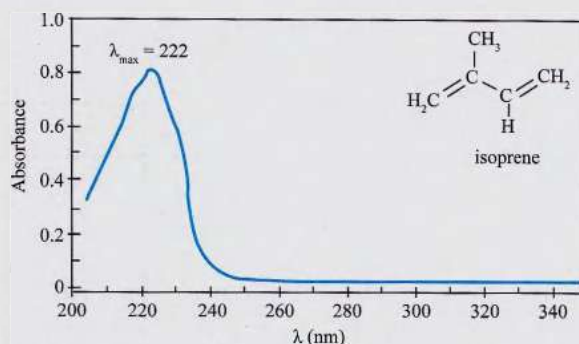
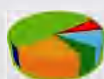


Fig. 25.1

Typical uv absorption spectrum of a conjugated alkene, isoprene.



ABSORPTION BY ORGANIC MOLECULES

Only some types of organic molecules absorb in the ultraviolet-visible region of the spectrum. The wavelengths at which an organic molecule absorbs depend on how tightly its electrons are bonded. Electrons in unsaturated bonds and non-bonded pairs absorb in the ultraviolet-visible region because they are relatively loosely held and are easily excited at these wavelengths.

When atoms combine to form molecules, the electrons in the atomic orbitals form molecular orbitals. Electrons may occupy sigma (σ) orbitals, pi (π) orbitals or non-bonding orbitals. When a σ bond or a π bond is formed a higher unfavourable energy level called an **anti-bonding orbital** is formed along with the bonding orbital. Anti-bonding orbitals are given the symbols σ^* and π^* . Atomic orbitals with lone pairs or non-bonding orbital are



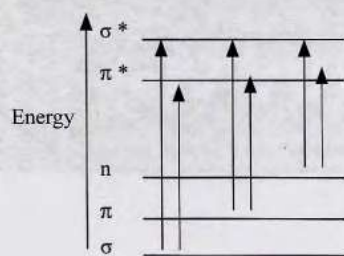


Fig. 25.2
Possible electron transition in molecular orbitals.

given the symbol n . Molecules in the ground state generally have electrons in the bonding and non-bonding orbitals. Absorption of energy can promote an electron from one of the filled σ , π or n orbital to an anti-bonding σ^* or π^* orbital.

Fig. 25.2

Of all the possible transitions only $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ normally produce absorption in the ultraviolet and visible region, the others require much more energy. Thus only molecules with π and or n electrons give characteristic ultraviolet or visible spectra. Molecules like alkanes will show no absorption in these regions since electrons are only in σ orbitals and transitions from $\sigma \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ require energy greater than that of ultraviolet radiation. The structural features of organic molecules which cause absorption of ultraviolet and visible wavelengths are called **chromophores**.

Table 25.1

Common chromophores and their approximate absorption maxima.

Chromophore	Typical λ max	Transitions
alkene $C = C$	175	$\pi \rightarrow \pi^*$
conjugated alkene $C = C - C = C$	220	$\pi \rightarrow \pi^*$
alkyne $C \equiv C$	180 (large ϵ_{max}) 225 (small ϵ_{max})	$\pi \rightarrow \pi^*$
carbonyl $C = O$	185 280	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
carboxyl $COOH$	205	$n \rightarrow \pi^*$
amide $CONH$	215	$n \rightarrow \pi^*$
azo $N = N$	340	$n \rightarrow \pi^*$
nitro NO_2	280	$n \rightarrow \pi^*$
nitrate NO_3	270	$n \rightarrow \pi^*$
alcohol OH	180	$n \rightarrow \sigma^*$

Increasing the extent of delocalization in a system containing double bonds increases the intensity of the absorption and shifts the position of absorption to a longer wavelength. Conjugated compounds have alternating double and single bonds which result in more delocalized electrons, therefore less energy is required for a $\pi \rightarrow \pi^*$ transitions. If the degree of conjugation is sufficient, absorption can take place in the visible region of the spectrum and the compound may appear coloured. For example, the $C=C$

double bond in ethene absorbs at 175 nm whereas β -carotene which has eleven double bonds absorbs at 450 nm causing it to appear bright orange.



Fig. 25.3



ABSORPTION BY TRANSITION METAL COMPLEXES

Transition metal ions show a wide range of colours. Most of them form complexes when surrounded by coordinating groups called ligands. The interaction between the ligands and the d orbitals of the metal ion causes the d orbitals to have different energies.

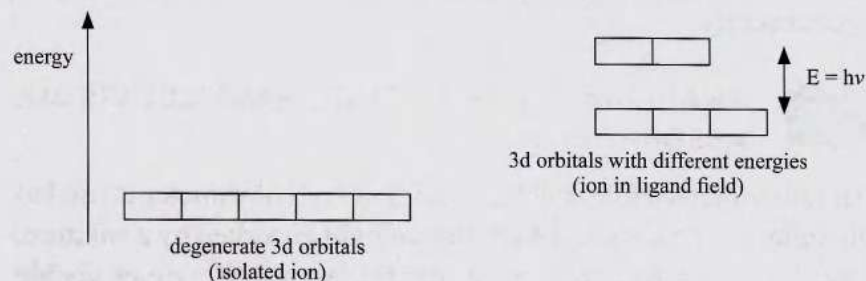


Fig. 25.4 Splitting of d orbitals

The energy E is required for d-d transitions and is in the visible region of the spectrum. Therefore coloured complexes are formed when electrons move from one d orbital to another. The colour of the complex is a complement of the colours absorbed from the visible light. It must be noted that ions with d^0 or d^{10} arrangement have no d-d transition possible and hence appear colourless.

Colourless compounds

Colour intensity is used to determine the concentration of a sample in ultraviolet-visible spectroscopy. However colourless compounds do not absorb visible light and cannot be quantified by direct measurement. In many cases the colourless sample is reacted with a colouring agent to form a highly coloured complex which absorbs visible light. The colouring agent contains a group which can be attached to the chromophore to modify both the wavelength and intensity of its absorption. This group is called an **auxochrome**. Many auxochromes contain N or O which possess lone pairs of electrons which may be promoted into the π^* anti-bonding orbital of the chromophore.



A colouring agent used in the analysis of iron is 1, 10 – phenanthroline. The iron in the sample is dissolved in acid and reduced to Fe^{2+} . It is then added to 1, 10 – phenanthroline to form an intense red coloured complex which absorbs at 512 nm.

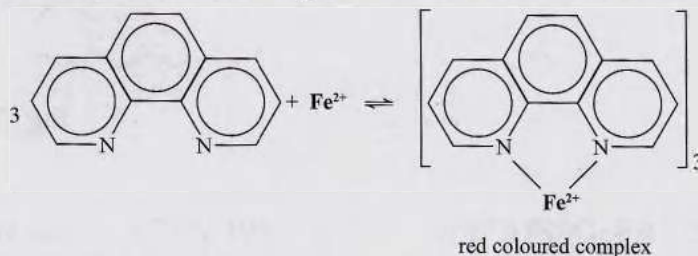


Fig. 25.5 1,10 – phenanthroline in analysis of iron

Similarly ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ can react with colourless phosphate to form a blue complex in SnCl_2 solution, thus allowing phosphate to be determined by uv-visible spectroscopy.



ANALYZING SAMPLES BY ULTRAVIOLET-VISIBLE ABSORPTION

An ultraviolet-visible spectrophotometer or colorimeter is used to quantitatively measure the amount of light absorbed by a solution. The basic components of a double-beam ultraviolet-visible spectrophotometer are a light source, a monochromator, a beam splitter, sample and reference cells, a detector and an amplifier. The light source is a deuterium or tungsten lamp which supplies a constant amount of light to the sample. The monochromator selects the required wavelength to be absorbed by the sample. The cell or cuvette is a transparent plastic or glass container for the sample or reference. The beam splitter divides the light into two paths, one passes through the sample cell and the other passes through the reference cell. Both paths meet at the detector which compares the two beams and records it.

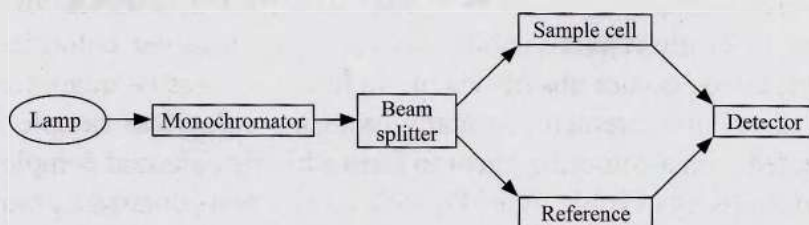


Fig. 25.6 Layout of a uv spectrophotometer

To find the concentration of an unknown sample, the instrument is first set at zero absorbance using a blank sample. Then a series of standard solutions of known concentrations are prepared. The absorbance of each solution and the unknown sample are then measured at a known maximum wavelength. A graph of

absorbance versus the known concentration of the series of standards is plotted to generate a calibration curve. The calibration curve is then used to determine the concentration of the unknown sample.

Beer-Lambert Law

The intensity of light exiting a solution, (I), is less than the intensity entering the solution, (I_0), because solute molecules absorb some of the energy. The amount of energy absorbed can be expressed in terms of either the transmittance (T) or the absorbance (A). The transmittance is simply the ratio of the exiting to the incoming radiation

$$T = \frac{I}{I_0}$$

It is often expressed as a percentage

$$\%T = \frac{I}{I_0} \times 100$$

Unfortunately, transmittance is not proportional to the concentration of the absorbing species, thus absorbance which is proportional to the concentration is used.

$$A = -\log T = \log \frac{I_0}{I}$$

If there is no absorption of light at a given wavelength, the percentage transmittance is 100 and the absorbance is 0. However, if the sample absorbs all of the light, the percentage transmittance is 0 and absorbance is infinity.

A relationship between the light absorbed by a compound and its concentration was derived by Beer and Lambert, which is extremely convenient for quantitative analysis of concentration. This relationship is referred to as **Beer-Lambert law** which states that the degree of absorption at a given wavelength of an absorbing compound in a non absorbing solvent depends on the concentration of compound and the path length of the radiation. This can be written as

$$A = \epsilon cl$$

Where A is the absorbance, ϵ is the molar absorptivity constant in $\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}$, c is the concentration in mol dm^{-3} and l is the cell length in cm.

Since the intensity of the incident light is decreased after passing through the sample, absorbance can also be expressed as



$$A = \log \frac{I_0}{I} = \epsilon cl$$

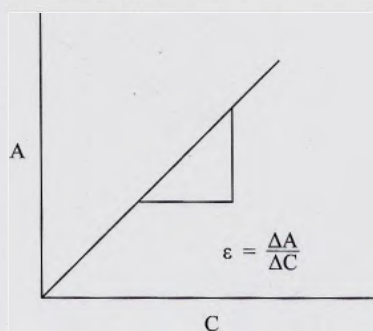


Fig. 25.7

Relationship between absorbance and concentration.

Where I_0 is the intensity of the incident light and I is the intensity of the emerging light.

When the cell length is 1 cm, a plot of absorbance versus concentration shows that the amount of light absorbed is directly proportional to the concentration of the compound absorbing it. The slope is ϵ and its value is an indication of the sensitivity of the method. Once ϵ has been determined for a particular species, the concentration can be calculated directly from the absorbance.

Fig. 25.7

Beer-Lambert law is generally obeyed for dilute solutions. It is assumed that absorbing species behave independently of the solvent and neighbouring molecules. Concentrations that are greater than 0.01 mol dm^{-3} can lead in interactions between neighbouring molecules resulting in a change in the absorbance characteristics of molecules. In addition, the law only holds for light of a single wavelength or narrow band of wavelengths.

Standard addition method (spiking)

This method is usually used to determine the concentration of an analyte in a complex mixture such as biological fluids or soil samples. These mixtures may contain other components that interfere with the analyte signal which can give an inaccurate value for the concentration. The technique involves adding a set of standard solution containing the analyte to equal volumes of the sample (spiking the sample) and monitoring the change in the instrument signal. The signal is measured for each spiked sample and the data is used to plot a calibration curve. The slope (ϵ) and the y-intercept (absorbance of sample) are used to calculate the concentration of the analyte in the sample using Beer-Lambert law. It is assumed that the change in the signal between the sample and the spiked samples is due only to the change in the analyte concentration.



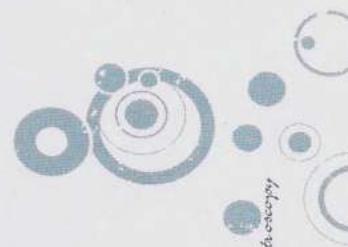
APPLICATIONS OF ULTRAVIOLET-VISIBLE SPECTROSCOPY

Qualitative applications of ultraviolet-visible spectroscopy are useful in detecting chromophoric groups. Unknown groups in a compound can be identified by comparing the spectrum with those of molecules containing various chromophoric groups.



However sufficient details for it to be used alone to identify a compound is not evident and data must be supplemented with other information such as infrared or mass spectra.

Quantitative analysis is widely used to determine the concentration of both organic and inorganic molecules such as glucose and urea in blood, iron in iron tablets and cyanide in water. This method is highly sensitive and can detect substances in the range of parts per million. Very often a wavelength can be found at which the analyte alone absorbs making the method moderately selective. In addition, measurements have good accuracy and are easily performed with modern instruments.





Questions

1. Explain the origin of absorption in ultraviolet-visible spectroscopy.
2. Explain why some organic species would absorb light in the ultraviolet-visible region whereas other would not.
3. Outline the basic steps involved in analyzing a sample by ultraviolet-visible spectroscopy.
4.
 - (a) Define Beer-Lambert law.
 - (b) A 1 cm^3 sample of a solution X showed an absorbance of 0.82 at a wavelength of 240 nm. Given the absorptivity constant is 12 000 and the cell path is 1 cm, calculate the molar concentration of X in the 1 cm^3 sample.
 - (c) State the limitations of Beer-Lambert law.
5. Explain the meaning of the following terms:
 - (a) chromophore
 - (b) auxochrome
 - (c) spiking
6. Nitrite in water can be determined by its reaction with sulphanilimide and N-(1-naphthyl)ethylenediamine to give a pink-coloured complex. Five standard solutions of nitrite were prepared, the pink colour was developed and the absorbances were recorded at 550 nm as shown in the table below.

[Nitrite]/ppm	Absorbance
2	0.010
4	0.020
6	0.031
8	0.041
10	0.050

- (a) Plot a calibration curve from the data given.
 - (b) Determine by interpolation of the calibration curve, the nitrite concentration of an unknown sample which gave an absorbance of 0.035.
 - (c) Using Beer-Lambert law, calculate the molar absorptivity (ϵ) assuming that the cell path is 1 cm.
7. Explain how UV-VIS spectroscopy can be used to distinguish between $\text{CH}_3\text{CH}(\text{OH})\text{CHO}$ and $\text{CH}_3\text{CH}_2\text{COOH}$.





ORIGIN OF ABSORPTION

Infrared radiation is not energetic enough to cause electronic transitions but it can induce vibrational and rotational transitions within the ground electronic state of the molecule. Absorption in the rotational levels may give rise to a series of peaks for each vibrational state. However rotation is often prevented in solid or liquid samples and the effects of these energy changes are not detected. Thus infrared spectra show closely spaced absorption peaks resulting from transitions among the various vibrational energy levels. Absorption of infrared wavelengths can cause bonds to stretch, bend or twist in characteristic ways. The energies associated with stretching vibrations are different from one another and that of bending or twisting vibrations. A molecule can vibrate in a number of ways which is related to the number of atoms and hence the number of bonds in the molecule.

Not all bonds within a molecule absorb energy at infrared wavelengths even though the frequency of the radiation exactly matches that of bond vibration. Only those bonds which have a dipole are capable of absorbing infrared radiation. The molecule absorbs only those infrared wavelengths that match vibrations that cause a change in dipole moment of the molecule. Symmetrical bonds such as those in H_2 or Cl_2 do not absorb infrared radiation because stretching does not change the dipole moment and bending cannot occur with only two atoms in a molecule. Infrared spectra for diatomic or triatomic molecules are relatively easy to understand, however absorption spectra become much more complex as the number of atoms in the molecule increase. This is due to the increase in the number of possible vibrations.

Vibrations can be divided into two types, depending on whether the bond length or angle is changing.

- Bond length change results in stretching (symmetric and asymmetric)
- Bond angle change results in bending (scissoring, rocking, wagging and twisting)

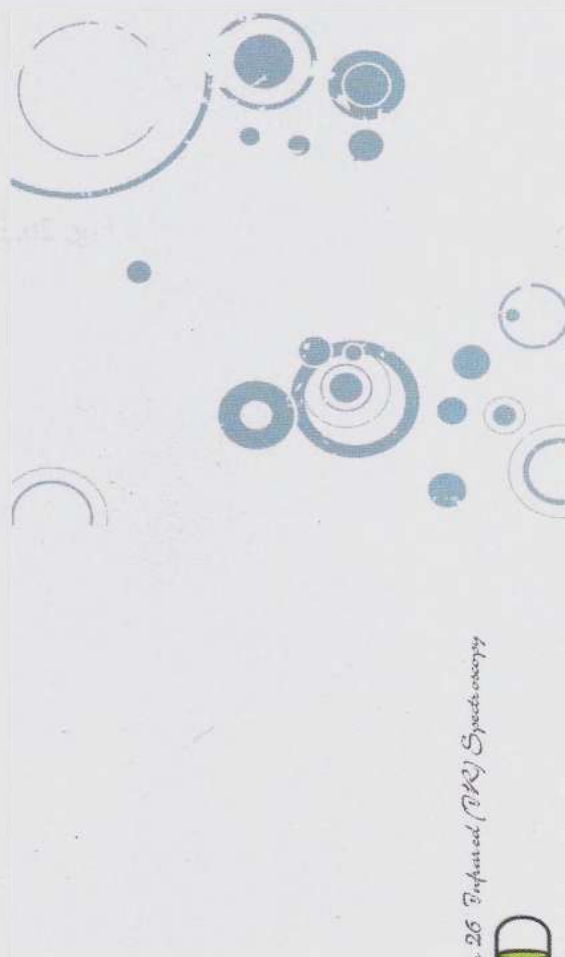
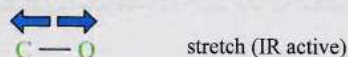
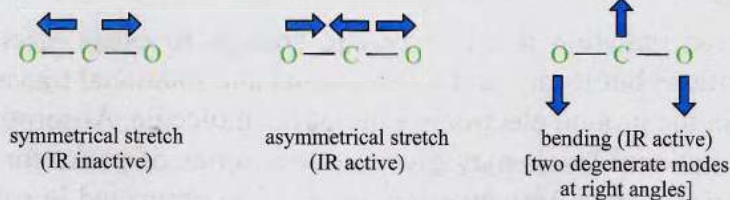


Fig. 26.1 and Fig. 26.2 below show the fundamental vibrations in carbon monoxide, carbon dioxide and sulphur dioxide.

Fig. 26.1 (a) Carbon monoxide



(b) Carbon dioxide



The two degenerate modes are equal-energy bending vibrations in CO_2 . They are identical except that one bending mode is in the plane of the paper, and one is out of the plane.

Fig. 26.2 Sulphur dioxide

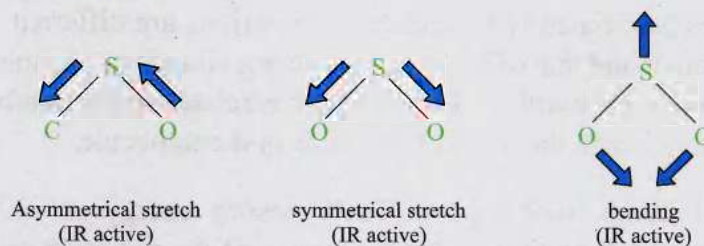
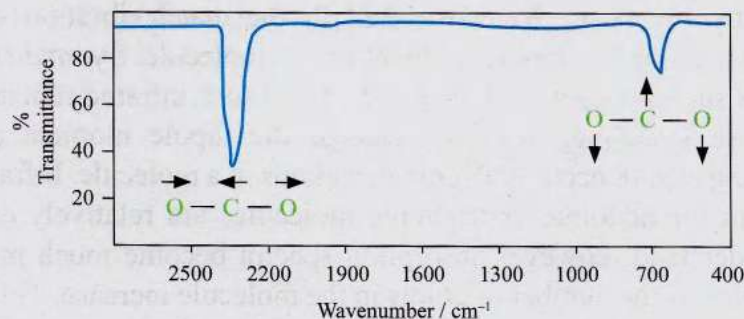
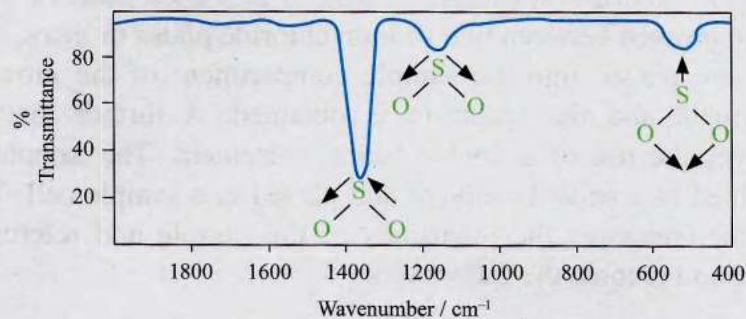


Fig. 26.3 IR spectrum of gaseous CO_2



Carbon dioxide shows only two absorption peaks. The symmetrical stretch of CO_2 causes no change in dipole thus no absorption occurs.

Fig. 26.4 IR spectrum of gaseous SO_2



Sulphur dioxide shows three absorption peaks. A change in dipole occurs in both stretching and bending.



ANALYZING SAMPLES BY INFRARED SPECTROSCOPY

The basic general design of an infrared spectrophotometer is similar to that of a double beam ultraviolet-visible spectrophotometer. However in infrared instruments, the infrared sources are heated inert solids and the cell compartment can be located between the radiation source and the monochromator. This arrangement is advantageous because the infrared radiation is not energetic enough to bring about photodecomposition which may occur if samples are exposed to an ultraviolet-visible source. Scattered radiation generated in the cell compartment may also be removed by the monochromator.

Most modern infrared spectrometers are of the Fourier transform infrared (FT-IR) variety which makes use of a mathematical function known as a Fourier transformation. A Fourier transform infrared (FT-IR) spectrometer passes several wavelengths through the sample at the same time and all the wavelengths are detected and measured simultaneously. It has the advantage of high sensitivity and speed (an entire spectrum can be obtained in less than 1 second).

Samples for investigation by infrared spectroscopy may be solids, liquids or gases. Solid samples may be analyzed by different methods. One method is to mix the sample with powdered potassium chloride or bromide and a portion of this mixture is compressed under vacuum into a disc. The disc is inserted into a sample holder and placed in the sample compartment in the infrared instrument. The result of the sample run is recorded as a plot of transmittance versus **wavenumber** (1/wavelength). Wavenumber is measured in cm^{-1} .



Another method is to mix the solid sample into a thick paste in a drop of paraffin oil (nujol). A drop of this thick paste or mull is then pressed between two sodium chloride plates or discs. The discs are placed into the sample compartment of the infrared instrument and the spectrum is obtained. A further method involves the use of a double beam instrument. The sample is dissolved in a suitable solvent and placed in a sample cell. The detector compares the intensities of the sample and reference beams and records the differences.

Analysis of liquid samples can be done by placing a drop of the sample between two sodium chloride plates or in a special liquid cell which is then inserted into the sample compartment. Usually the liquid sample is diluted to a concentration of about 0.2 mol dm^{-3} using a suitable organic solvent such as carbon tetrachloride or carbon disulphide. Water is not used to prepare samples because it may damage the sodium chloride plates or cells.

Gases are usually analyzed in a special cell which has a path length of about 10 cm and end walls made of sodium chloride. The cell is placed in the beam of infrared radiation.



INTERPRETING INFRARED SPECTRA

An infrared absorption spectrum consists of a wide range of narrow absorption peaks with wavenumbers from 4000 cm^{-1} to about 600 cm^{-1} . A typical infrared spectrum can be visually divided into two regions, the **bond spotting** and **fingerprint** regions. The bond spotting region occurs in the shorter wavelength region, about wavenumbers 4000 cm^{-1} to 1200 cm^{-1} , and usually contains few peaks. This region is useful to identify different functional groups within a molecule. The position of the peaks due to certain bonds usually occurs in the same region of the spectrum regardless of the structure of the rest of the molecule.



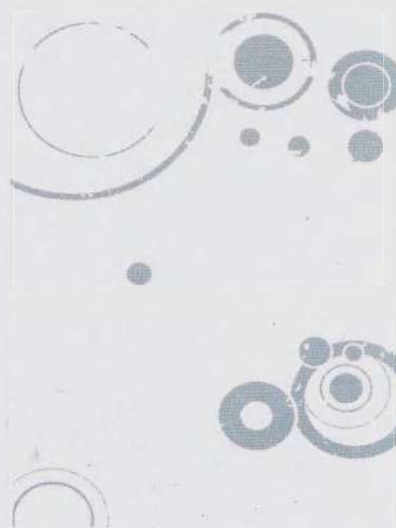
Table 26.1

The positions of characteristic absorption peaks for some common functional groups.

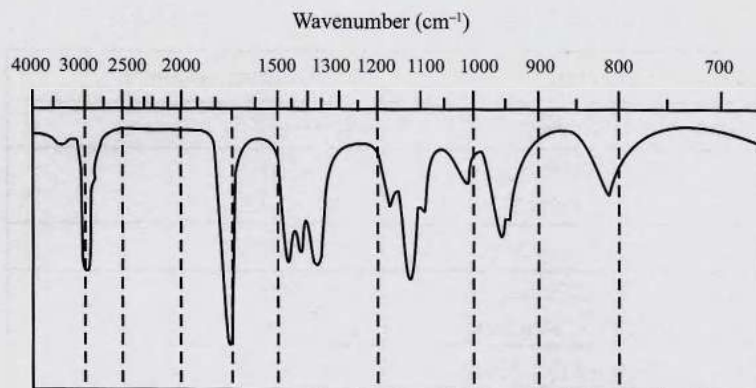
Functional Group	Wavenumbers (cm^{-1})
Alkyl C – H Stretch	2950 – 2850
Alkene C – H Stretch	3100 – 3010
Alkene C = C Stretch	1680 – 1620
Alkyne C $\equiv$ C Stretch	2260 – 2100
Aromatic C – H Bending	860 – 680
Aromatic C = C Bending	1700 – 1500
Alcohol/Phenol O – H Stretch	3550 – 3200
Carboxylic Acid O – H Stretch	3300 – 2500
Amine N – H Stretch	3500 – 3300
Amide N – H Stretch	3700 – 3500
Nitrile C $\equiv$ N Stretch	2280 – 2220
Aldehyde C = O Stretch	1740 – 1690
Ketone C = O Stretch	1725 – 1680
Ester C = O Stretch	1750 – 1730
Carboxylic Acid C = O Stretch	1740 – 1700
Amide C = O Stretch	1690 – 1640

The remaining infrared region normally consists of many peaks of varying intensities, many of which are not readily identifiable. This complex region is known as the **fingerprint region** because almost every organic compound produces a unique pattern in this area. Therefore identity of a compound can often be confirmed by comparing this region to that of a known spectrum.

It must be noted that if a reference infrared spectrum is not available for an unknown molecule, then infrared spectroscopy does not provide sufficient details for it to be used alone to identify a molecule. Although systemic examination can be used for structure elucidation, identification of the functional groups in a molecule is rarely sufficient to allow positive identification of the compound.



Example 1

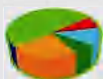


The spectrum of the compound above shows the following:

3400-3200 cm^{-1}	no OH or NH present
3100 cm^{-1}	no peak to suggest unsaturated CH
2900 cm^{-1}	strong peak indicating saturated CH
2200 cm^{-1}	no unsymmetrical triple bonds
1710 cm^{-1}	strong carbonyl absorbance
1610 cm^{-1}	no absorbance to suggest carbon-carbon double bonds

Alkane C-H bonds are usually less useful in determining structure as most organic molecules contain C-H bonds.

The spectrum appears to be consistent with a simple aliphatic carbonyl compound.



APPLICATIONS OF INFRARED SPECTROSCOPY

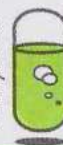
Infrared spectroscopy is a less satisfactory technique for quantitative analysis when compared to ultraviolet-visible spectroscopy because deviations from Beer-Lambert law are common and infrared absorbance measurements are less precise. However where modest precision is adequate, the uniqueness of an infrared spectrum has particular application in the analysis of a variety of chemical compounds. Infrared photometers are used to monitor the concentration of a variety of air pollutants such as carbon monoxide, carbon dioxide and sulphur dioxide. This method is sensitive, rapid and highly specific for a variety of compounds.





Questions

1. Explain the origin of absorption in infrared spectroscopy.
2. Outline the basic steps involved in the analysis of each of the following samples by infrared spectroscopy:
 - (a) a solid sample
 - (b) a liquid sample
 - (c) a gas sample
3.
 - (a) Explain how infrared spectroscopy can be used to distinguish between functional groups in organic molecules.
 - (b) Use infrared spectroscopy to distinguish between the following compounds:
 - (i) $\text{CH}_3\text{CH}_2\text{COOH}$ and $\text{CH}_3\text{CH}_2\text{OH}$
 - (ii) $\text{CH}_3\text{CH}=\text{CHNH}_2$ and $\text{CH}_3\text{CH}=\text{CHCN}$
 - (iii) $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ and $\text{C}_6\text{H}_5\text{COOH}$
4. Explain why three characteristic absorption peaks are seen in an IR spectrum of sulphur dioxide but only two peaks are seen in that of carbon dioxide.
5. Discuss the significance of the bond spotting and the fingerprint regions of the IR spectrum.



As described earlier, the mass spectrometer is used to determine the relative atomic mass and the relative abundance of isotopes. A sample to be analyzed is vaporized and bombarded with a stream of high energy electrons producing positive ions which are accelerated in an electric field. The high speed positive ions are deflected in a magnetic field and separated according to their mass to charge ratio. Ions with a particular mass to charge ratio are detected and recorded as a mass spectrum. The relative heights of the peaks in the mass spectrum give a measure of the relative amounts of the different ions present.



FRAGMENTATION

Mass spectroscopy is also used to analyze organic molecules. The beam of electrons used for ionization in the mass spectrometer may also cause the molecular ion to break into fragments. Fragmentation of the molecular ion occurs readily at positions that give the most stable carbocation fragments. When fragmentation occurs one fragment retains the positive charge while the other fragment is often electrically neutral. Only the positively charged fragments appear in the spectrum. The fragments give information about the structure of the original molecule. The fragment in greatest quantity produces the tallest peak and is called the **base peak**. All the other peaks in the spectrum are measured as a percentage of the abundance of the base peak.



THE MOLECULAR ION PEAK

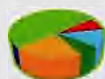
When one electron is lost from the complete molecule, the peak produced is called the **molecular ion peak, (M)**. The mass of this peak represents the relative formula mass of the molecule. The molecular ion peak is usually found among the peaks of greatest mass in the spectrum but is not necessarily the peak with the highest mass since various isotopes may be present in the molecule. In cases where the molecular ion is not stable, the peak may appear weak or may even be absent. This is because the molecular ion fragments into more stable carbocation fragments and does not exist long enough for a peak to appear.



THE M + 1 PEAK

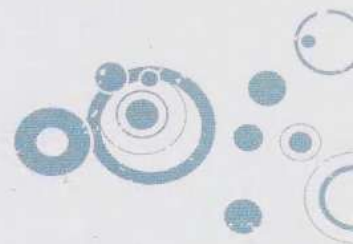
A peak with a mass 1 unit heavier than the molecular ion is called the **M+1 peak**. This may be due to the presence of ^{13}C or ^2H isotopes in some of the molecules. The ^{13}C isotope is considered to be the major contributor to the M+1 peak because the relative abundance of ^{13}C in nature is 1 % of that of ^{12}C while that of ^2H is 0.01 % of that of ^1H . So for a butane molecule, C_4H_{10} , the occurrence of a mass 1 unit heavier than the molecular ion will be 4×1 or 4 % of the time for ^{13}C and 10×0.01 or 0.1 % of the time for ^2H . This means that if the M+1 peak was caused by an isotope of carbon, it would have a relative abundance of 4 % of that of the molecular ion peak. On the other hand, if it was caused by an isotope of hydrogen then it would have a relative abundance of 0.1 % of the molecular ion peak. In the mass spectrum of butane, the M+1 peak is about 4 % of that of the molecular ion peak which suggests that the M+1 peak may be due to one of the ^{12}C atoms being replaced by a ^{13}C atom.

The presence of the M+1 peak can be used to determine the number of carbon atoms present in a molecule. This is significant in distinguishing between unknown molecules which have similar relative molecular masses. For example, both $\text{C}_3\text{H}_8\text{O}$ and $\text{CH}_4\text{N}_2\text{O}$ have similar relative molecular masses but both have a different number of carbon atoms. The relative abundance of the M+1 peak can be used to determine the number of carbon atoms in each molecule and hence distinguish between the two molecules.



M + 2 PEAK

Some compounds produce a peak with a mass 2 unit heavier than the molecular ion. This is called the **M+2 peak** and is often caused by the presence of chlorine or bromine atom. The relative abundance of ^{37}Cl in nature is 33 % that of ^{35}Cl so that the mass spectrum of a compound containing a chlorine atom produces an M+2 peak that is about one third the relative abundance of the molecular ion peak. Similarly the natural abundance of ^{81}Br is 98 % of that of ^{79}Br , thus the mass spectrum of a compound containing a bromine atom produces an M+2 peak that is almost equal to the molecular ion peak.

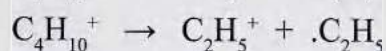




FRAGMENTATION PATTERNS

It is important to realize that the mass spectrum of an organic compound gives quite different information from the mass spectrum of an element. With an element, each line represents a different isotope of that element, whereas with an organic compound, each line represents a different fragment produced when the molecular ion breaks up.

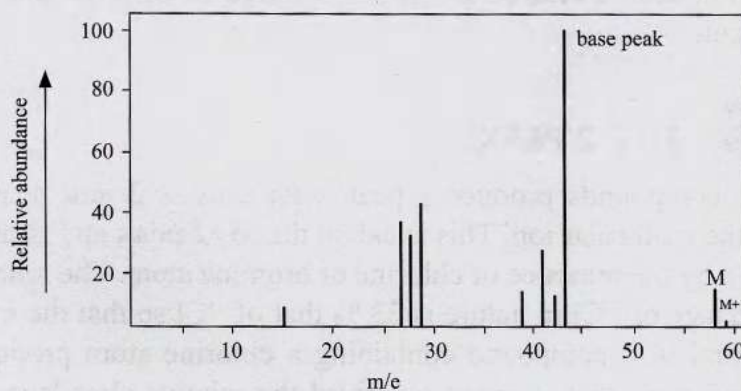
The fragmentation pattern of butane shown in Fig. 27.1 below produces peaks with mass/charge ratio of 15, 27, 28, 29, 39, 41, 42, 43, 58 and 59. The most stable ion (C_3H_7^+) occurs at $m/e = 43$ which is the base peak. The molecular ion ($\text{C}_4\text{H}_{10}^+$) is present at $m/e = 58$ and the $M+1$ peak is at 59. The peaks at m/e ratio 15 and 29 are the CH_3^+ ion and C_2H_5^+ ion respectively. These are produced by fragmentation as shown below.



The other peaks in the spectrum are produced by the loss of one or more hydrogen atoms from these fragments. Occasionally unexpected peaks appear in the mass spectrum. This is usually an indication that some form of molecular rearrangement has occurred within the instrument.

Fig. 27.1

Mass spectrum of butane

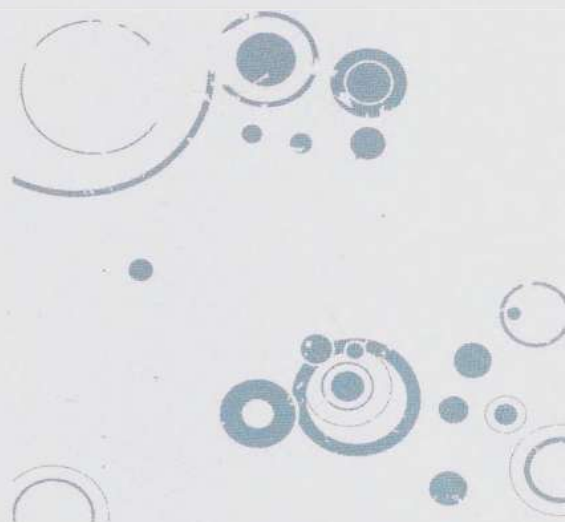




APPLICATIONS OF MASS SPECTROSCOPY

The combination of mass spectrometry and gas chromatography makes a powerful tool for the detection of trace quantities of substances in forensic science. Mass spectroscopy is used

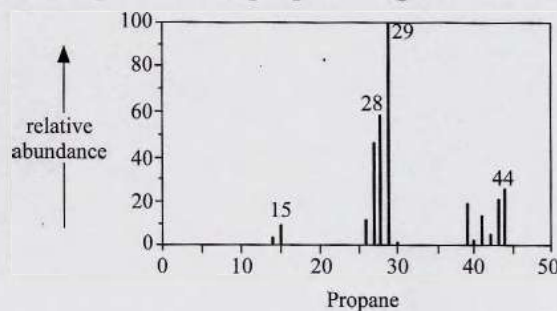
- to determine relative isotopic masses and relative isotopic abundance.
- to distinguish between molecules of similar relative molecular mass.
- to identify compounds based on their fragmentation patterns.
- in carbon and other radioactive dating processes.
- by satellites and spacecraft to identify particles intercepted in space.





Questions

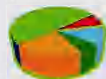
1. Define the following terms:
 - (a) Molecular ion
 - (b) $M + 1$ peak
 - (c) Base peak
2.
 - (a) In the mass spectrum of 2-methylbutan-2-ol, peaks appear at m/e values of 56, 59, 71 and 73. Suggest a molecular formula for each of the peaks shown.
 - (b) Explain why the molecular ion peak did not appear on the mass spectrum of 2-methylbutan-2-ol but it appeared on the mass spectrum of its isomer pentan-2-ol?
3.
 - (a) Briefly explain how a mass spectrometer works to obtain a mass spectrum of a molecule.
 - (b) The mass spectrum of propane is given below.



Identify the following peaks in the spectrum:

- (i) Molecular ion peak
- (ii) Base peak
- (iv) Suggest a possible identity for the species corresponding to the mass of 29.





ORIGIN OF NMR

Nuclear magnetic resonance (NMR) spectroscopy is based on the magnetic property of the nucleus of an atom. Nuclei which contain an odd number of protons or neutrons behave like tiny magnets when placed in a magnetic field. This is because protons and neutrons possess the property of spin as displayed by electrons. Just as electrons with opposite spins pair up, protons pair up with other protons of opposite spin. Neutrons also do the same. Since the spin of the electron on its axis can be clockwise or anti-clockwise and is described by the spin quantum numbers $-\frac{1}{2}$ and $+\frac{1}{2}$, the spin of a proton or neutron is described in the same way.

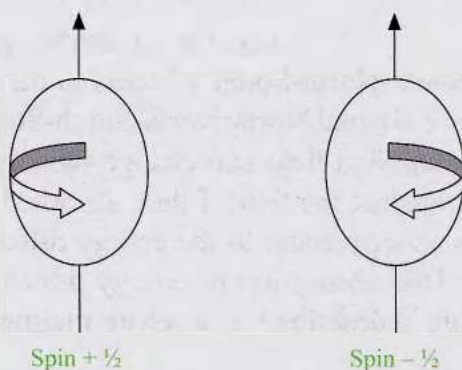


Fig. 28.1 Spin of proton or neutron

Thus an unpaired protons or neutrons will have a net spin of $\frac{1}{2}$, this will result in the nucleus having a spin momentum which will give rise to a magnetic moment. Paired particles, with opposite spin, will have a net spin of zero and therefore no magnetic moment. Table 28.1 below shows the net spin of some nuclei.

Nuclei	Unpaired Protons	Unpaired Neutrons	Net Spin
^1H	1	0	$\frac{1}{2}$
^2H	1	1	1
^{13}C	0	1	$\frac{1}{2}$
^{19}F	1	0	$\frac{1}{2}$
^{23}Na	1	2	$\frac{3}{2}$
^{31}P	1	0	$\frac{1}{2}$

Table 28.1

It must be noted that nuclei can have more than one unpaired proton or neutron just as the electronic structures in transition metals can have many unpaired spins.

Spin behaviour in a magnetic field

The spin states of a nucleus are degenerate i.e. they all have the same energy. However when a magnetic nucleus is placed in a magnetic field, the spin states are no longer of the same energy. The magnetic moment of the nucleus may align itself with or against the applied magnetic field just like a magnet and in doing so, the spin states split into two different energy levels as shown in fig. 28.2.

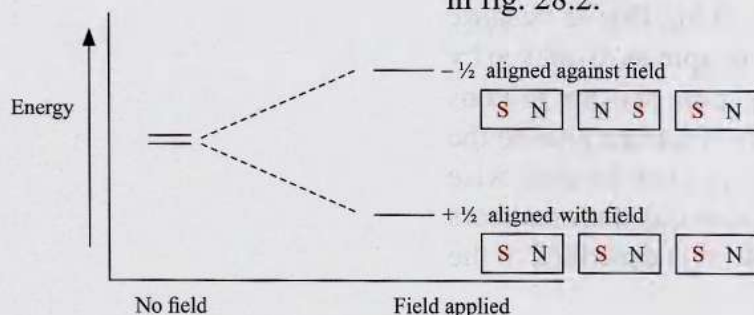


Fig. 28.2

Fig. 28.2

The spin state in which the nuclear magnetic moment is aligned with the applied field is at a lower energy level than that which is aligned against the field. In the lower energy state, the nuclear magnetic poles are

aligned North-South-North-South whereas in the higher energy state, the poles are aligned North-North-South-South. The nuclei aligned with the applied field can change their spin state (**flip**) to that which is against the field if they absorbed a quantum of energy which is exactly equal to the energy difference between the spin states. This absorption of energy which flips the spin state of a nucleus is described as **nuclear magnetic resonance (NMR)**.

The energy difference between the two spin states is much smaller than the energy differences between the electronic, vibrational and rotational energy levels. For typical applied magnetic fields, the energy difference between the two spin states corresponds to the **radiofrequency region** of the electromagnetic spectrum. Since this energy is very small, it is influenced by minor differences in environment. Therefore the quantum of energy absorbed for the nuclear spin to flip depends on the environment of the nucleus concerned (i.e. the other nuclei and electrons around it) and the strength of the applied magnetic field. Thus NMR spectroscopy can utilize nuclear spin flip energies to determine chemical structures. NMR applied to the ^1H nucleus is referred to as **proton NMR** or **^1H NMR**. It is widely used to determine the structure of unknown organic compounds because most organic compounds

contain ^1H nuclei. NMR spectroscopy in the following sections deals specifically with ^1H nuclei.



NMR SPECTROMETER

The basic structure of a typical NMR spectrometer consists of a sample tube which is spun on its axis between the poles of an electromagnet. Around the sample tube is a coil which is connected to a radiofrequency oscillator which supplies the energy for the nuclear spin to flip. A second coil is connected to a detector which is attached to an amplifier and recorder. See fig. 28.3.

Fig. 28.3

The NMR spectrometer is tuned to the specific nucleus that is being measured (e.g. ^1H). The sample is dissolved in a solvent which has no protons, e.g. tetrachloromethane (CCl_4) and a small amount of tetramethylsilane, $\text{Si}(\text{CH}_3)_4$ (also referred to as **TMS**) is added to the sample to act as an internal standard. If no energy is being absorbed by the sample, the detector coil picks up none of the energy from the oscillator coil. However when energy is absorbed by the sample and the nuclear spin flips, a signal is induced in the detector coil and is recorded as a resonance signal. The resonance frequency of each proton in the sample is compared to the resonance frequency of the protons in the TMS.

Fourier transform NMR spectrometers can speed up the time taken to acquire a scan by allowing a range of frequencies to be probed at once. This technique uses a mathematical function known as a Fourier transformation to analyze a complex waveform and work out the amplitudes of each single frequency component in it. This analysis is performed by a computerized system within the instrument which then plots a spectrum.

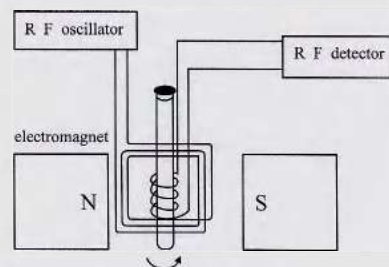


Fig. 28.3

Layout of NMR spectrometer



NMR spectrometer





CHEMICAL SHIFT AND TMS

Protons in different chemical environments (surrounded by different groups such as -OH , -CH_3 and -CHO) do not experience the same applied magnetic field. This is because electrons are charged particles and move in response to the external magnetic field so as to generate a secondary field that opposes the much stronger applied field. This secondary field shields the nucleus from the applied field, thereby reducing the effective magnetic field. The greater the shielding effect, a larger applied field is required to allow the shielded protons to come into resonance at a fixed frequency.

When electronegative groups are attached to the molecule, the electron density is decreased around the protons and there is less shielding. The nucleus is **deshielded** and feels a stronger magnetic field thus a lower applied field would be required to bring protons into resonance. The extent of shielding or deshielding differs for each type of hydrogen and depends on the electron density around the hydrogen. Therefore the nature of protons in an organic molecule can be determined either by measuring the magnetic field strengths that will cause absorption at a fixed frequency, or by measuring the frequencies at which the molecule absorbs radiation in a fixed magnetic field. It is more practical to vary the magnetic field strengths because only relatively small changes in the magnetic field strength are required.

The modification of the applied field which causes protons in different chemical environment to resonate at different field strengths is referred to as the **chemical shift**. This is measured on a delta (δ) scale and is usually expressed in parts per million (ppm) by frequency from the **TMS** (tetramethylsilane) reference point.

$$\delta = \frac{\text{observed shift from TMS} \times 10^6 \text{ (Hz)}}{\text{operating frequency of the spectrometer (Hz)}}$$

The proton signal from the -CH_3 group in TMS is used as a reference point for ^1H NMR and is assigned the chemical shift of zero. TMS is chemically inert, non-toxic and volatile. It is used because the protons of the compound are more shielded than most compounds known and gives a single, intense resonance signal away from the proton signals normally found in organic compounds. This is because all 12 protons in TMS are in the same chemical environment and experience the same magnetic field.



Most common organic molecules show a chemical shift in the range of 0–10 δ . Protons that are shielded have a lower chemical shift and are said to resonate **upfield**. These shielded protons result in resonance signals that appear at the right of a spectrum. Protons that are deshielded have higher chemical shift and are said to resonate **downfield** and appear at the left of a spectrum.

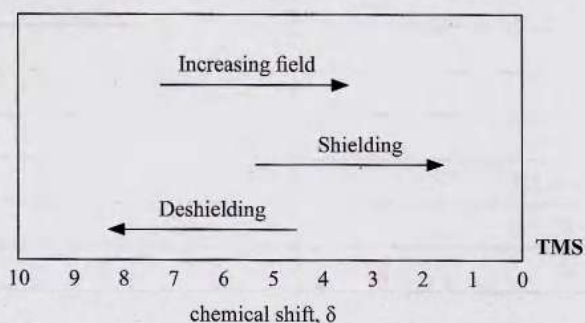


Fig. 28.4 Position of shielded and deshielded protons in NMR spectrum

Chemical shift shows the chemical environment of each proton. The spectrum of $C_4H_8O_2$ shows the chemical environment of each proton.

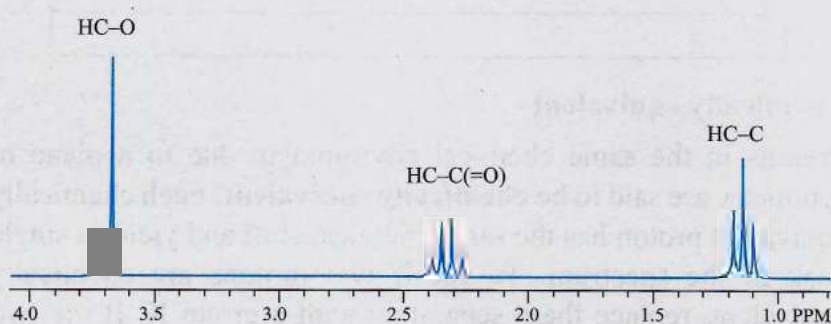


Fig. 28.5 NMR spectrum of $C_4H_8O_2$



Table 28.2 Typical chemical shifts values in proton NMR spectra

Structure	chemical shift (ppm)
RCH_3	0.8 – 1.2
R_2CH_2	1.1 – 1.5
R_3CH	~1.5
$ArCH_3$	2.2 – 2.5
R_2NCH_3	2.2 – 2.6
R_2CHOR	3.2 – 4.3
R_2CHCl	3.5 – 3.7
$RC(=O)CHR_2$	2.0 – 2.7
$RCH=CR_2$	~1.7
$RC=CH$	4.9 – 5.9
ArH	6.0 – 8.0
$RC(=O)H$	9.4 – 10.4
$RCCH$	2.3 – 2.9
R_2NH	2 – 4
ROH	1 – 6
$ArOH$	6 – 8
RCO_2H	10 – 12

Chemically equivalent

Protons in the same chemical environment due to a plane of symmetry are said to be **chemically equivalent**. Each chemically equivalent proton has the same chemical shift and yields a single peak in the spectrum. To see if two protons are chemically equivalent, replace them separately with a group X. If the two products are identical then the protons are equivalent. If the two products are not identical, then the protons are not equivalent. For example, if H^a in bromomethane is replaced by X, the product is the same as when H^b is replaced by X. This indicates that H^a and H^b are equivalent protons.

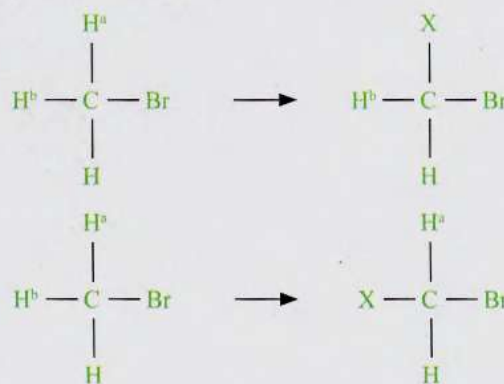


Fig. 28.6
Chemically equivalent
protons

However if H^a in bromoethane is replaced by X, the product is not the same as when H^b is replaced by X. This indicates that H^a and H^b are not equivalent protons.

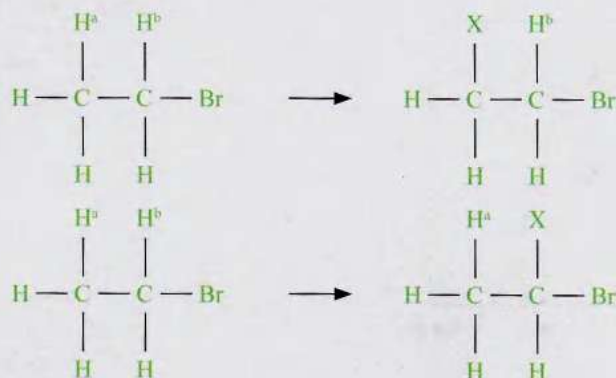


Fig. 28.7
Not chemically
equivalent protons

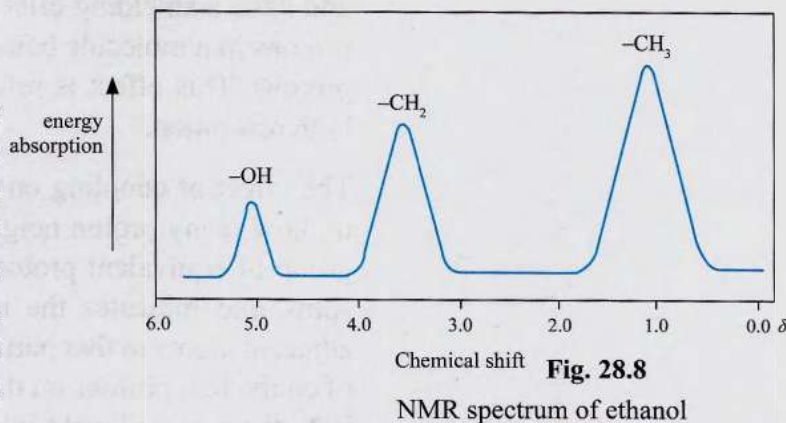


INTERPRETING NMR SPECTRA

The value of a chemical shift in an NMR spectrum gives information about a proton and its environment. Each peak in the NMR spectrum represents a proton in a particular environment. For example, the low resolution NMR spectrum of ethanol shows three different chemical shift values which suggest that protons are in three different chemical environments. These correspond to the protons in the $-OH$, $-CH_2$ and $-CH_3$ part of the molecule.

Fig. 28.8

The spectrum also shows the peaks are of different sizes. The areas under these peaks are proportional to the number of protons in that particular environment. The areas under the three peaks are in a ratio 1:2:3 which correspond to one proton in $-OH$, two protons in $-CH_2$ and three protons in $-CH_3$.



Chemical shift **Fig. 28.8**
NMR spectrum of ethanol

The area under the peak is calculated automatically by the instrument and is displayed as an **integration trace** above each peak. The height of the step of the integration trace is proportional to the area under the peak. It gives the relative ratio of the number of protons for each peak. Fig. 28.9 shows the spectrum of ethoxyethane, $C_2H_5OC_2H_5$, which has two peaks and the steps on the integration trace are in a ratio of 2:3. Since there are 10 protons, this suggests that there are a set of 4 and a set of 6 equivalent



protons. The 4 equivalent protons are from the two $-\text{CH}_2$ groups and the 6 equivalent protons are from the two $-\text{CH}_3$ groups.

► Fig. 28.9

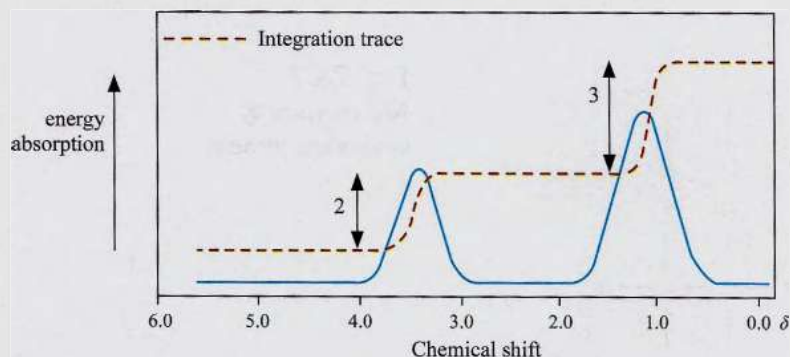
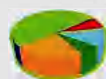


Fig. 28.9

NMR spectrum of ethoxyethane



SPIN-SPIN SPLITTING

At high resolution, a single peak by a given group of equivalent protons is often seen to split into multiple peaks. This is because their magnetic fields are close enough to interact and influence the protons up to three bonds away. Therefore a neighbouring proton can have its magnetic field aligned with the applied field and have a slightly deshielding effect or aligned against the applied field and have a shielding effect. This results in the chemical shift of protons in a molecule being slightly changed by other equivalent protons. This effect is referred to as **coupling** and is evident at high resolution.

The effect of coupling on the NMR spectrum gives information on how many proton neighbours exist for a particular proton or group of equivalent protons. The number of parts a single peak splits into indicates the number of equivalent protons on the adjacent atoms to that particular proton. In general, if the number of equivalent protons on the adjacent atoms of a particular proton is N , the peak will split into $N + 1$ peaks. This means

- **no protons** on the adjacent atoms, the peak will remain a single peak (a **singlet**).
- **one proton** on the adjacent atoms, the peak will split into two closely spaced peaks of equal size (a **doublet**).
- **two protons** on the adjacent atoms, the peak will split into three closely spaced peaks with an area in the ratio of 1:2:1 (a **triplet**).
- **three protons** on the adjacent atoms, the peak will split into four closely spaced peaks with an area in the ratio of 1:3:3:1, (a **quartet**).



The ratios of the areas under the peaks can be worked out by a mathematical relationship called Pascal's triangle. Each number in the triangle is the sum of the two numbers above it to the left and right as shown in fig. 28.10.

Fig. 28.10

Consider the spectrum of ethanol at high resolution in fig. 28.11 there is no splitting of the peak from the single $-\text{OH}$ proton which suggests that there are no protons on the adjacent atom. The peak from the two $-\text{CH}_2$ protons splits into a quartet which suggests that there are three protons on the adjacent atoms, that is, a $-\text{CH}_3$ neighbour.

The peak from the three $-\text{CH}_3$ protons splits into a triplet, this suggests that there are two protons on the adjacent atoms, that is, a $-\text{CH}_2$ neighbour. Thus the structure of ethanol must have a $-\text{CH}_3$ with a $-\text{CH}_2$ neighbour, a $-\text{CH}_2$ with a $-\text{CH}_3$ neighbour and an $-\text{OH}$. Hence the structure worked out for ethanol is $\text{CH}_3\text{CH}_2\text{OH}$.

Number of chemically equivalent protons causing splitting	Ratio of the peaks in the splitting pattern
0	1
1	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1
5	1 5 10 10 5 1
6	1 6 15 20 15 6 1

(Pascal's triangle)

Fig. 28.10

Fig. 28.11

^1H NMR spectroscopy thus gives information about

- the number of different types of protons in the molecule (the number of peaks)
- the electronic environment of the different types of protons (chemical shift values)
- the ratio of the different types of protons giving rise to the various signals (integration trace)
- the number of proton neighbours that exist for a particular proton (spin-spin splitting)

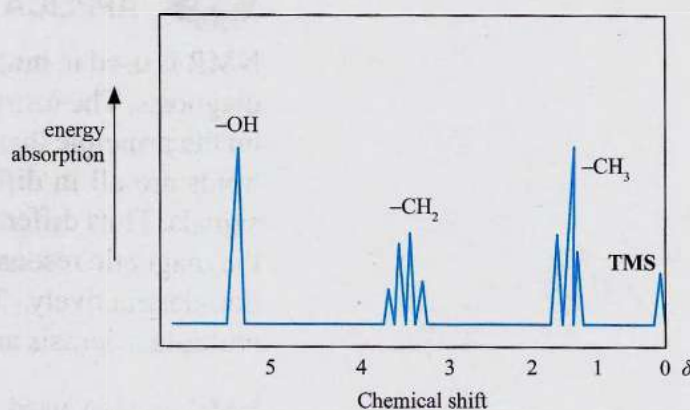


Fig. 28.11

Spectrum of ethanol at high resolution

Magnetically equivalent

Chemically equivalent protons that have the same resonance frequency and do not split each other at high resolution are said to be **magnetically equivalent**. Protons that are magnetically equivalent must have identical chemical shift and they must have the same coupling to other nuclei in the molecule. This means that at high resolution, a single peak by a given group of equivalent protons would not split if it is magnetically equivalent.

Identifying labile protons

Deuterium oxide ($^2\text{H}_2\text{O}$) is used in NMR to identify labile (easily removed) protons. Deuterium oxide is simply water in which the ^1H atoms are replaced by ^2H (deuterium) atoms. If deuterium oxide is added to the ethanol, the peak due to the $-\text{OH}$ proton reduces or disappears. This is because the ^2H proton from deuterium oxide exchanges easily with the labile proton of the $-\text{OH}$ group in ethanol as shown in the equation below.



Since ^2H (deuterium) does not undergo magnetic resonance, the peak due to $-\text{OH}$ disappears.



APPLICATION OF ^1H NMR SPECTROSCOPY

NMR is used in **magnetic resonance imaging (MRI)** for medical diagnosis. The instrument is called a body scanner which operates on the principle that protons in water, carbohydrates, proteins and lipids are all in different environment and give rise to different signals. Thus different organs in the body can be differentiated in the magnetic resonance image. It can analyze biological samples non-destructively. This technique is used to diagnose cancer, multiple sclerosis and many other diseases.

NMR is also used in the petroleum industry to determine the hydrocarbon present in oilfields and the structure of organic compounds.





Questions

1. Describe the property of the nuclei that causes them to be detected by NMR analysis.
2. Explain the following terms used in NMR:
 - (a) chemical shift
 - (b) chemically equivalent
 - (c) upfield
 - (d) deshielding
3. Explain the use of tetramethylsilane (TMS) as a standard reference substance in NMR spectroscopy.
4. A proton has a resonance of 150 Hz downfield from TMS on a spectrometer that operates at 75MHz. Calculate the chemical shift for the proton.
5. NMR analysis of an organic compound X of molecular formula $C_9H_{10}O$ shows five H at chemical shift 7.5, two H at chemical shift 3 and three H at chemical shift 1.2.
 - (a) Identify the functional groups indicated by the chemical shifts.
 - (b) Suggest a structure for compound X.



Chromatography is used to analyze small quantities of a mixture of substances which are chemically similar to each other. It involves the partition of the components of the mixture between a stationary phase and a mobile phase. The mixture to be separated is introduced into the stationary phase which stays still. The mobile phase is then allowed to move over the stationary phase for separation. Partition depends on the different solubilities of the components in the mobile phase and the different adsorption forces of the components with the stationary phase. **Adsorption** is the temporary attraction of molecules of a gas or liquid to a solid surface. Components with greater solubilities will dissolve in the mobile phase and move along with it readily. Components with stronger adsorption forces will be held on the stationary phase and not move along readily with the mobile phase. The differences in solubilities and adsorption bring about separation.



PAPER CHROMATOGRAPHY

In paper chromatography, a piece of filter paper or chromatography paper is used which consists of stationary water molecules embedded in a cellulose matrix. The paper acts as the stationary phase. The mobile phase consists of a suitable solvent that travels up the stationary phase. The mixture to be separated is spotted a short distance from one end of the paper (the **base line**). The end below the spot is placed in the solvent. As the solvent moves along the paper it carries the mixture with it. The distance the solvent moves from the baseline is called the **solvent front**. Components of the mixture will separate readily according to how strongly they adsorb on the stationary phase and how readily they dissolve in the mobile phase.

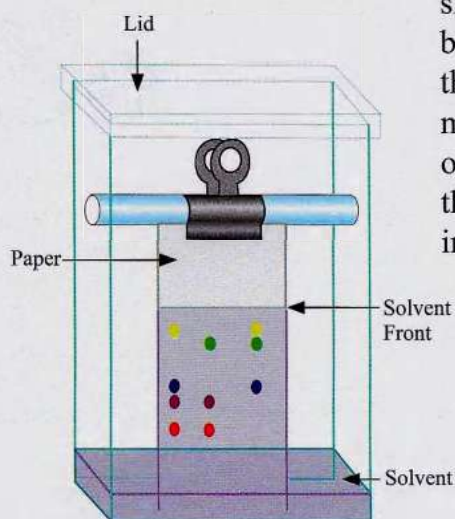


Fig. 29.1

If the separated components are colourless, then a visualizing agent can be used to convert them into coloured spots. The positions of certain substances can also be determined by fluorescing under a UV lamp.

Fig. 29.1

A paper chromatography system

The ratio of the distance moved by a component of the mixture to the distance moved by the solvent is called the retention factor,



R_f

$$R_f = \frac{\text{distance moved by a component}}{\text{distance moved by solvent}}$$

Each component has a characteristic R_f value for a given solvent under controlled conditions. Thus R_f values of known substances can be used to identify components of a mixture.

Paper chromatography is used to analyze mixtures such as dyes in ink, colouring in food additives and amino acids from protein hydrolysis. A visualizing agent such as ninhydrin is used to detecting amino acids and amines.



THIN LAYER CHROMATOGRAPHY (TLC)

This method is similar to paper chromatography. The stationary phase is a thin layer of powdered alumina or silica gel which is fixed on to a glass or plastic plate. Plates can be coated with a slurry of the powdered adsorbent and then oven-dried. The mixture to be analyzed is spotted near the bottom of the plate. The end below the spot is placed in a suitable solvent. This solvent is the mobile phase and moves up the plate causing the components of the mixture to partition between the adsorbent on the plate and the moving solvent. The separated components may be recovered for further analysis by scraping spots off the plate.

Thin layer chromatography has the advantage that a variety of adsorbents can be used for separation. It is commonly used to separate amino acids in blood samples and for analysis of food dyes.



COLUMN CHROMATOGRAPHY

This method is similar to thin layer chromatography however the stationary phase is packed into a vertical glass column (diameter 1 – 2 cm) instead of being coated on to a plate. A slurry of silica gel or alumina is commonly used for column chromatography. The mixture to be analyzed is applied to the top of the column. The mobile phase is a suitable solvent which is added to the top of the loaded column. The solvent flows down the column under gravity causing the components of the mixture to partition between the adsorbent and the solvent. Each component emerges from the column at different times and can be collected separately.

The time between addition of the sample at the top of the column



and the emergence of a component at the bottom of the column is called the **retention time** of that component. Identical substances will have the same retention time under the same conditions thus retention times can be used to identify substances.

Column chromatography has the advantage that larger quantities can be separated and therefore can be used to prepare compounds in addition to analyzing them. This method is used in biochemical research and in hospitals to identify amino acids, peptides and nucleotides.

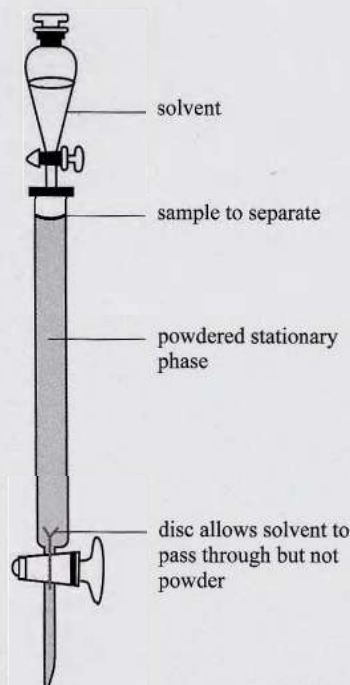
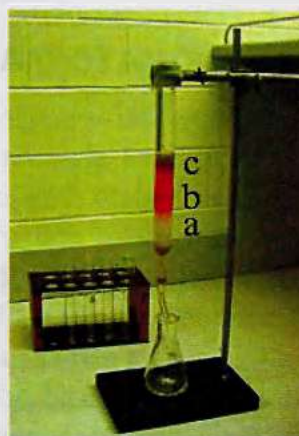


Fig. 29.2
The apparatus for column chromatography

Fig. 29.2



Components a, b, and c separate down the column



HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

This technique is similar to column chromatography however instead of gravity feed, high pressure is used to force the solvent through the column. Columns are smaller than those used in column chromatography, some being 10 cm to 30 cm long and 4 mm in diameter. Retention times are shorter thus rapid analysis of substances can be made. HPLC is used in the industry and hospitals. It is also used to identify suspected stimulants, doping and drugs that may be present in athletes and racehorses.

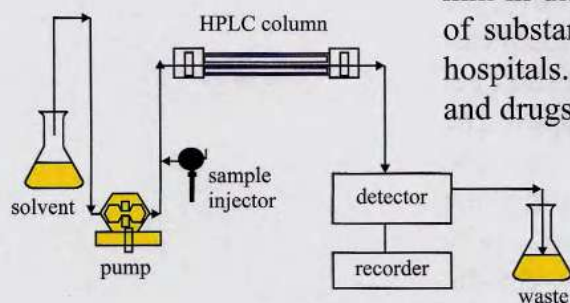


Fig. 29.3
The components of a HPLC system

Fig. 29.3





GAS-LIQUID CHROMATOGRAPHY (GLC)

GLC uses a longer column than HPLC. It is usually packed with the stationary phase which is an inert powder coated with an involatile oil. The column is maintained at a constant, pre-set temperature in an oven. The mobile phase is an unreactive gas, usually nitrogen or helium and is referred to as the carrier gas. The sample to be analyzed has to be in the vapour state at the temperature at which the column is operated. The vaporized sample is carried through the column by the mobile phase. The sample is partitioned between the oil and the carrier gas. A detector records each component as it leaves the column at different times. Emerging components can also be fed directly into a mass spectrometer for identification.

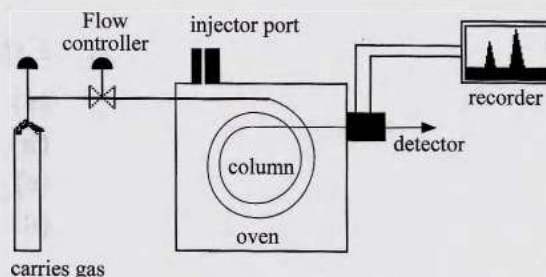


Fig. 29.4

The components of a GLC system

Fig. 29.4

Fig 29.5 shows the chromatogram for analyte X which has three peaks. Peak A is the signal that corresponds to the solvent and it has a retention time of 2 minutes. Peak B and C correspond to the two components in the separated mixture. B has a retention time of 4 minutes while C has one of 6 minutes. The area under the peak is proportional to the concentration of the component in the mixture.

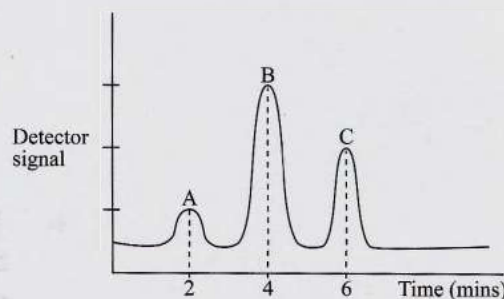


Fig. 29.5

Fig. 29.5

GLC method of analysis is very sensitive and can be used in forensic testing, to monitor air and water pollution, to detect and identify traces of pesticides or agricultural chemicals in foodstuff and to check dosage of drugs in blood or urine samples.





Questions

1. Explain the principles upon which chromatography are based.
2. Explain the following terms:
 - (a) retention factor
 - (b) retention time
 - (c) solvent front
 - (d) visualizing agent
3.
 - (a) Distinguish between the stationary and the mobile phase in chromatography.
 - (b) Give one example of a stationary phase and a mobile phase used in each of the following chromatographic methods:
 - (i) thin layer
 - (ii) column
 - (iii) gas-liquid
4. Two different brands of purple food colouring are analyzed by paper chromatography. Both samples contained a blue pigment. In the first sample, the solvent travelled 8.25 cm while the blue pigment travelled 5.68 cm. In the second sample, the solvent travelled 7.86 while the blue pigment travelled 5.41 cm.
 - (a) Calculate the retention factor of the blue pigment in each sample.
 - (b) Is it a different blue pigment present in the two brands of the purple colouring?
Justify your answer.



When one liquid dissolves in another, it is possible to separate the mixture by fractional distillation. The principle is based on a law called Raoult's law.



RAOULT'S LAW AND IDEAL SOLUTIONS

In the 1880's Raoult found that for certain pairs of miscible liquids, the vapour pressure of either liquid at equilibrium was directly proportional to the mole fraction of that liquid in the mixture. This became known as Raoult's law and can be expressed as an equation. So for a pair of liquids A and B

$$P_A = P_A^\circ x_A$$

where P_A is the partial vapour pressure of A at equilibrium, P_A° is the vapour pressure of the pure A at that temperature and x_A is the mole fraction of A in the mixture.

The mole fraction of A is

$$x_A = \frac{n_A}{n_A + n_B}$$

where n_A and n_B are the number of moles of A and B respectively in the mixture.

From the expression it can be seen that when $x_A = 1$, liquid A is pure and the vapour pressure is entirely due to liquid A.

For gases, pressure P is proportional to the number of moles n , thus the mole fraction can be expressed in terms of pressure.

$$x_A = \frac{P_A}{P_A + P_B}$$

The vapour pressure-composition graph would be a straight line joining the vapour pressure of pure A and pure B as shown in Fig. 30.1 This shows the total vapour pressure of liquids A and B at any composition. The blue lines show the separate vapour pressures of A and B at any composition. The total vapour pressure

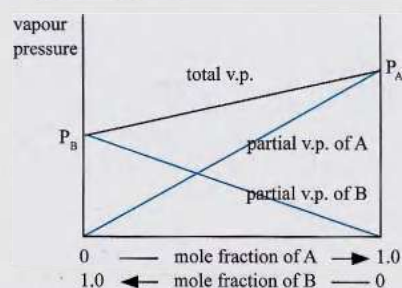


Fig. 30.1

Vapour pressure-composition graph of A and B



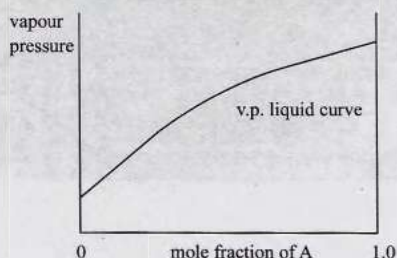


Fig. 30.2

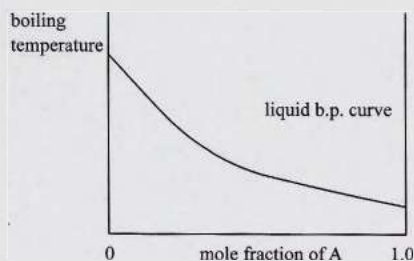


Fig. 30.3

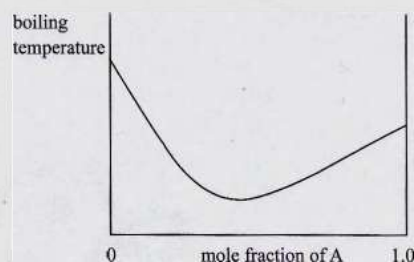


Fig. 30.4a

Minimum boiling point azeotrope

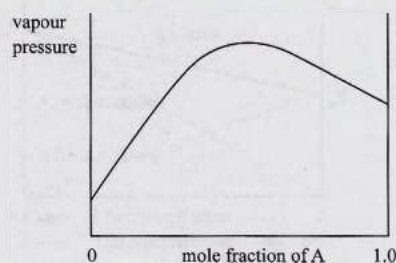


Fig. 30.4b

Maximum vapour pressure

will be the combined vapour pressure of liquids A and B.

$$P_{\text{total}} = P_A + P_B$$

Fig. 30.2

Raoult's law assumes that the intermolecular forces between A-A, B-B and A-B are similar and there is no enthalpy or volume change on mixing. Many pairs of liquids obey Raoult's law and are termed **ideal solutions**. Examples of ideal solutions are water and methanol both of which form hydrogen bonds, and hexane and heptane both of which form van der Waals bonds.

For ideal solutions, the vapour pressure-composition graph is a straight line however ideal solutions are relatively rare and the graph is rarely a straight line. The vapour pressure-composition graph is actually a curve for liquids which do not depart greatly from ideality as shown in fig. 30.2.

Fig. 30.3

Since vapour pressure is inversely related to boiling temperatures i.e. the higher the vapour pressure, the lower the boiling point, we can also plot a boiling temperature-composition graph as shown in fig. 30.3. Boiling temperatures are easier to measure than vapour pressures.

Fig. 30.4



NON-IDEAL MIXTURES

Positive deviation from Raoult's law

In some mixtures, the A-B interaction is weaker than the A-A or B-B interactions. As a result the molecules escape from the mixture more easily than for an ideal solution. Such a mixture shows a positive deviation from Raoult's law, for example hexane and ethanol. The positive deviation is great enough for there to be a maximum vapour pressure at a particular composition. This vapour pressure is greater than any other composition and either of the pure liquids. The same mixture will have a minimum boiling point lower than any other composition and either of the pure liquids. Such a mixture is called a **minimum boiling point azeotrope**. Fig. 30.4a shows a boiling temperature-composition graph of a minimum boiling point azeotrope while fig. 30.4b shows a vapour pressure-composition graph for a minimum boiling point azeotrope.



Fig. 30.5

Negative deviation from Raoult's law

In other mixtures, the A-B interaction is greater than the A-A and B-B interactions therefore it is more difficult for the molecules to escape from the mixture than for an ideal mixture. Such a mixture shows a **negative deviation** from Raoult's law. There is a minimum vapour pressure which is less than any other composition and either of the pure liquids. This means that there is a maximum boiling point which is higher than any other composition and either of the pure liquids. Such a mixture is called a **maximum boiling point azeotrope**, e.g. trichloromethane and ethyl ethanoate. The boiling temperature-composition graph and the vapour pressure-composition graph of a maximum boiling point azeotrope are shown in fig. 30.5(a) and (b).

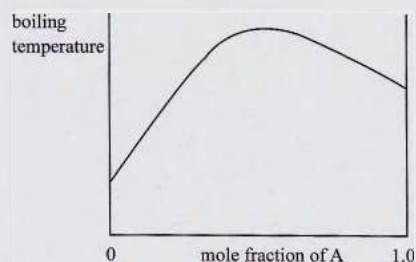


Fig. 30.5a

Maximum boiling point azeotrope

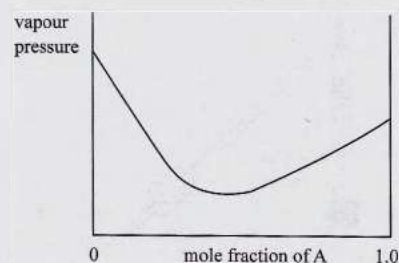


Fig. 30.5b

Minimum vapour pressure



PRINCIPLES OF FRACTIONAL DISTILLATION

Simple distillation can be used to separate a volatile liquid from a non-volatile solute as the vapour contains only the volatile component which can be condensed and separated. However fractional distillation is used to separate two liquids which are miscible and vary only slightly in volatility.

Consider two components A and B, of which A is slightly more volatile than B. The vapour pressure of A is 70 kPa and that of B is 30 kPa in a 1:1 equimolar solution at a certain temperature.

The partial vapour pressure of A = $P_A = 70 \times 0.5 = 35$ kPa

The partial vapour pressure of B = $P_B = 30 \times 0.5 = 15$ kPa

The mole fraction of A in the vapour = $\frac{P_A}{(P_A + P_B)} = \frac{35}{50} = 0.7$

The mole fraction of B in the vapour = $\frac{P_B}{(P_A + P_B)} = \frac{15}{50} = 0.3$

The liquid mixture in which the mole fraction of A is 0.5 has a vapour in which the mole fraction is 0.7. Hence the vapour is richer in component A which has the lower boiling point. This generally holds for ideal solutions at any composition. Fig. 30.6 shows how a liquid in which the mole fraction of A is 0.5 gives a vapour richer in A.

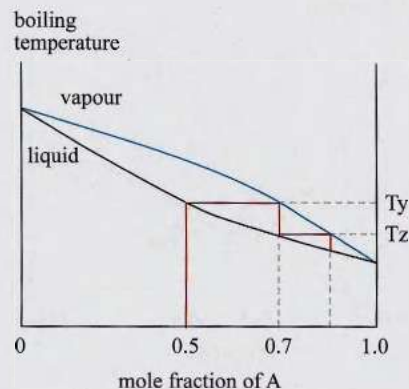


Fig. 30.6



The mixture of each liquid with mole fraction 0.5 has a boiling point of T_y and is in equilibrium with the vapour of mole fraction 0.7. On condensing the 0.7 mole fraction, A boils at a lower temperature T_z and gives a vapour even richer in component A.

This is the principle of fractional distillation in which condensation and vaporization continuously takes place in a fractionating column. Columns are long and densely packed to facilitate many successive condensation and vaporization. As the temperature decreases up the column, the vapour becomes richer in the more volatile component A until the vapour consists of pure A.

Fig. 30.7

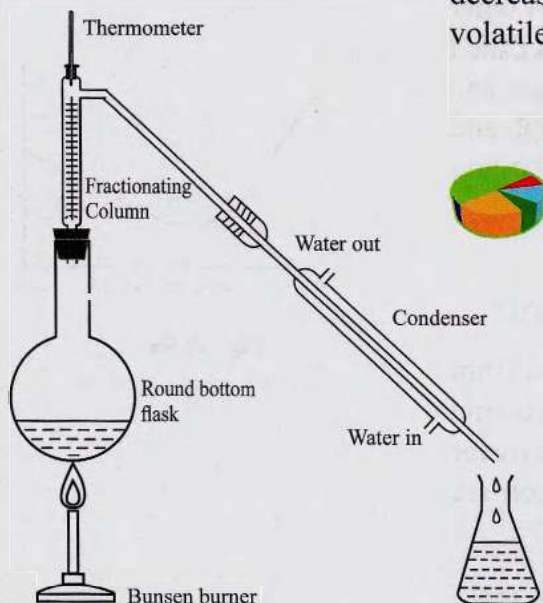


Fig. 30.7
Fractional distillation diagram



FRACTIONAL DISTILLATION OF NON-IDEAL SOLUTIONS

Azeotropes show different distillation behaviour from ideal solutions. For a minimum boiling point azeotrope, fractional distillation of a mixture of composition y and composition z is shown in the boiling point-composition curve in fig. 30.8 and summarized in table 30.1.

Table 30.1

Fractional distillation of a minimum boiling point azeotrope

Composition y		Composition z	
collects as distillate	remains in flask	collects as distillate	remains in flask
azeotrope	pure A	azeotrope	pure B

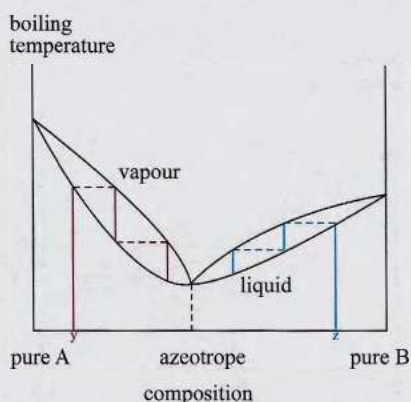


Fig. 30.8
A boiling point/composition curve for a minimum boiling point azeotrope

When a mixture of composition y undergoes fractional distillation, the mixture gets richer in the composition of the azeotrope (a specific composition of A and B). The azeotrope has a lower boiling point than pure A and distills off leaving pure A in the distilling flask. When a mixture of composition z undergoes fractional distillation, the azeotrope distills off and pure B remains in the distilling flask. These mixtures cannot be fully separated by fractional distillation.

Fig. 30.8

For a maximum boiling point azeotrope, fractional distillation of two separate samples of a mixture of composition y and



composition z is shown in the boiling point-composition curve in Fig. 30.9 and summarized in table 30.2.

► **Fig. 30.9**

Table 30.2

Fractional distillation of a maximum boiling point azeotrope

Composition y		Composition z	
collects as distillate	remains in flask	collects as distillate	remains in flask
pure A	azeotrope	pure B	azeotrope

When a mixture of composition y undergoes fractional distillation, a pure sample of A distills off leaving the azeotrope (a specific composition of A and B) in the distilling flask. When a mixture of composition z undergoes fractional distillation, pure B distills off and the azeotrope remains in the distilling flask.



VACUUM DISTILLATION

Vacuum distillation is simple distillation at reduced pressures (below one atmosphere). Reduced pressure results in lower boiling points. Many compounds cannot be distilled at atmospheric pressure because their boiling points are too high or they decompose before reaching their normal boiling points. Some of these substances can be distilled under reduced pressure because their boiling temperature can be lowered significantly. Also reduced pressure decreases the energy requirement for both the heating and cooling processes.



STEAM DISTILLATION

Steam distillation is a technique that has significant commercial applications. It is commonly used to extract essential oils from natural products, for example eucalyptus oil from eucalyptus, eugenol from cloves, citrus oils from lemon or orange peel, and to extract oils used in perfumes from various plant materials. It is an ideal way to separate organic compounds which tend to decompose before reaching their boiling temperatures.

Steam is introduced into the distillation apparatus. As the hot steam passes through the mixture it releases heat which may be enough to boil the mixture provided the volume of the mixture is not too great. For larger volumes, it is better to heat the flask so that too much steam would not condense in the mixture and

boiling
temperature

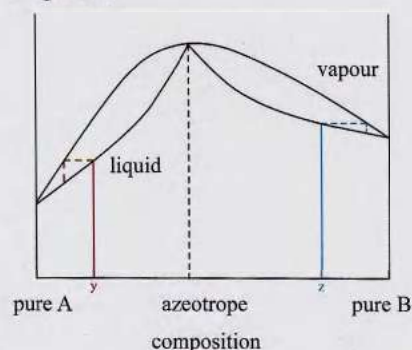
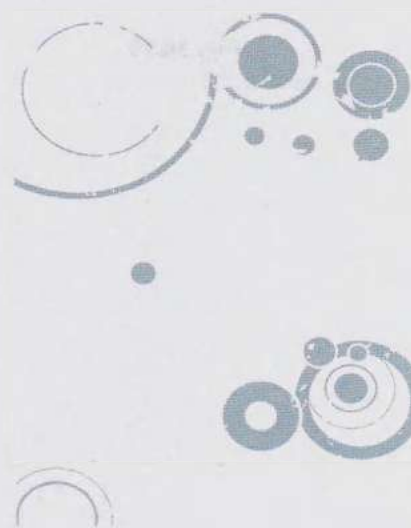


Fig. 30.9

A boiling
point /composition curve for
a maximum boiling point azeotrope



cause the volume of liquid in the flask to become too much. The mixture boils at a lower temperature and distills to give a two layer system of water and the organic compounds. The two layers are separated using a separating funnel and purified using a suitable drying agent to remove the water

Steam distillation operates on the principle that immiscible liquids each exert their own vapour pressure so that when the mixture boils the sum of the vapour pressure is equal to one atmosphere. Therefore the mixture distills below the temperature at which the vapour pressure of the pure liquid would reach one atmosphere.

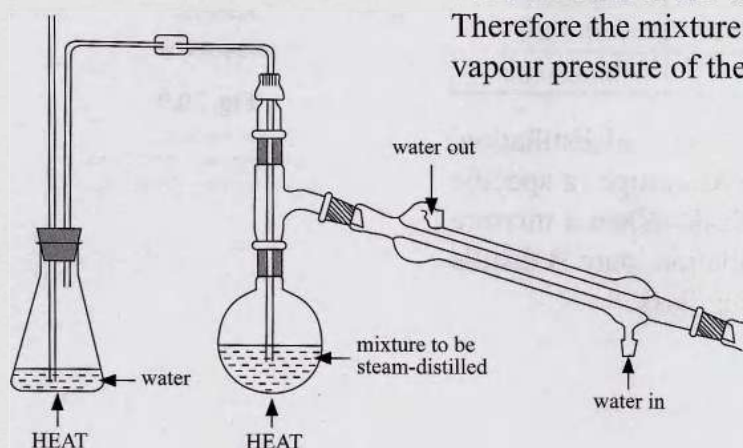


Fig. 30.10

Fig. 30.10

steam distillation apparatus



SOLVENT EXTRACTION

Solvent extraction is a technique used to separate compounds based on their preferential solubilities for two different immiscible solvent. This process allows the separation of a substance due to its unequal solubilities in two immiscible liquid. It involves the partial removal of a solute from one liquid in which it is less soluble to another immiscible liquid in which it is more soluble. Since the two liquids are immiscible, they are easily separated using a separating funnel.

If a solute is shaken with a mixture of two immiscible solvents at a fixed temperature, the dissolved solute distributes itself such that its concentration in the two layers will be in a fixed ratio. The term partition is used when the solute distributes itself between the two immiscible liquids.

Consider a system where solute X is distributed between two immiscible solvents, aqueous and organic.



The concentration of the solute in each solvent at equilibrium is a constant ratio and the equilibrium constant for the system is called the **partition coefficient** which is given by



$$k = \frac{[X (\text{organic})]}{[X (\text{aqueous})]}$$

The partition coefficient is applicable only in dilute solutions and when the solute has the same molecular form in both solvents. The value of the partition coefficient depends on the solute and the two immiscible solvents, and like other equilibrium constants it varies with temperature.

Products of organic preparations are often dissolved in water. If the organic product is more soluble in an organic solvent, then solvent extraction can be used to separate the organic product from its aqueous solution. The technique involves shaking a sample of the aqueous solute together with a sample of an organic solvent in a separating funnel. The solute distributes itself between the two immiscible solvents. The tap is opened occasionally during the shaking to release any pressure caused by the solvent vapours. The organic layer is then separated from the aqueous layer and is dried with a suitable drying agent such as anhydrous magnesium sulphate. The solute is recovered by distilling off the organic solvent.

Ether is an organic solvent used in solvent extraction. It dissolves many organic compounds and is immiscible with water. It also has a low boiling point and can be distilled off easily from the extracted solution and recycled. However safety precautions must be taken when using or storing an organic solvent such as ether. It is flammable and the vapour is denser than air therefore distillation is carried out in a fume cupboard. Ether can also form unstable organic peroxides which are explosive thus it is stored over a reducing agent such as iron (II) sulphate crystals.

Solvent extraction is more efficient if a certain volume of the extracting solvent is used in several portions rather than one. Consider an aqueous solution which contains 8 g of solute A in 1 dm³ of water. Given the partition coefficient for solute A between ether and water is 66 we can calculate the mass of solute A extracted in (i) a single 100 cm³ portion of ether and (ii) two successive 50 cm³ portions of ether.

- (i) Let the mass of solute A extracted by 100 cm³ of ether = x Substituting the concentrations in the partition coefficient expression

$$\frac{\frac{x}{100}}{\frac{(8-x)}{1000}} = 66$$

$$x = 6.95 \text{ g}$$

The mass of solute A extracted by a single 100 cm³ of ether is 6.95 g.

- (ii) Let the mass of solute A extracted by the first 50 cm³ of ether = y



$$\frac{\frac{y}{50}}{\frac{(8-y)}{1000}} = 66$$

$$y = 6.14 \text{ g}$$

The mass of solute A extracted by the first 50 cm³ of ether is 6.14 g, hence 1.86 g of solute A now remain in the aqueous solution.

Let the mass of solute A extracted by the second 50 cm³ portion of ether = z

$$\frac{\frac{z}{50}}{\frac{(1.86-z)}{1000}} = 66$$

$$z = 1.43 \text{ g}$$

The total mass of solute A extracted by the two successive 50 cm³ samples of ether is

$$6.14 + 1.43 = 7.57 \text{ g}$$

This is more than the 6.95 g of solute A extracted using a single 100 cm³ volume of ether.

Calculating a partition coefficient

When a solution containing 2.0 g of solute X in 100 cm³ of water was shaken with 20 cm³ of ether, 1.6 g of X was extracted in the ether layer. Calculate the partition coefficient of X between the ether and water.

To calculate the partition coefficient between two solvents, the concentration of the first solvent mentioned goes on the numerator of the partition coefficient expression.

$$k = \frac{\text{concentration of X in ether}}{\text{concentration of X in water}}$$

$$= \frac{1.6 / 20}{0.4 / 100}$$

$$= 20$$

Although the square brackets represent concentration in mol dm⁻³, you can use concentration as mol dm⁻³ or g cm⁻³ once the same units are used in the numerator and denominator.



Questions

1. What do you understand by the following terms:
 - (a) Ideal solution
 - (b) Azeotrope
 - (c) Partition coefficient
2. Draw a boiling point-composition curve of an ideal solution and use it to explain the principles upon which fractional distillation are based.
3.
 - (a) Explain the chemical principles of the following:
 - (i) steam distillation
 - (ii) vacuum distillation
 - (b) What are the advantages of carrying out the processes in (a) (i)-(ii) above?
4.
 - (a) Define the term *partition coefficient*.
 - (b) List two conditions under which the partition coefficient remains constant.
 - (c) Benzene is immiscible with water. When 50 cm^3 of an aqueous solution containing 0.5g of an organic solute X is shaken with 5 cm^3 of benzene, 0.2g of solute X is extracted in the benzene. Calculate a value for the partition coefficient of X between benzene and water.
 - (d) If the aqueous layer from (c) above is shaken with a another 5 cm^3 of benzene, what mass of solute X will be extracted in the benzene when equilibrium is reached?
5. Sketch a boiling point-composition curve for a mixture of ethanol and benzene which forms an azeotrope at boiling point 68°C and mole fraction 0.32 of ethanol. The boiling point of ethanol and benzene is 78°C and 80°C respectively.



Recrystallization

Solid products may be purified by recrystallization from a suitable solvent. This process depends on the fact that most solids are more soluble in hot solvents than in cold, and that the impurities present will have different solubilities from the required compound.

Recrystallization involves dissolving the impure solid in a minimum amount of hot solvent. Insoluble impurities are removed by filtering the hot solution. The solution is allowed to cool so that crystals of the required compound are formed. The crystals are filtered, washed with a little cold solvent and dried. Soluble impurities remain in the filtrate at low temperatures.

Coloured impurities may be removed using an adsorbent such as finely divided charcoal. A small amount of charcoal is added to the hot solution followed by hot filtration to remove the charcoal. This removes coloured impurities but may also lead to product loss. Excess decolourizing agent should be avoided because it may adsorb appreciable amounts of the substance being purified.

To remove insoluble impurities and decolourizing agents, hot solutions must be filtered rapidly, otherwise the solution may cool and crystals may form prematurely. Rapid filtration is done using fluted filter paper or vacuum filtration.

A good recovery of purified material is obtained using the smallest amount of hot solvent. This minimizes the amount of product lost by retention in the mother liquor. Sometimes crystallization may not occur readily when the hot solution is cooled. In such cases, crystallization may be induced by scratching the sides of the flask with a glass rod beneath the surface of the solution or "seeding" the cold solution with a pure crystal of the substance being purified.





SELECTION OF SOLVENT

A good solvent must be selected if recrystallization is to be effective. A good solvent should

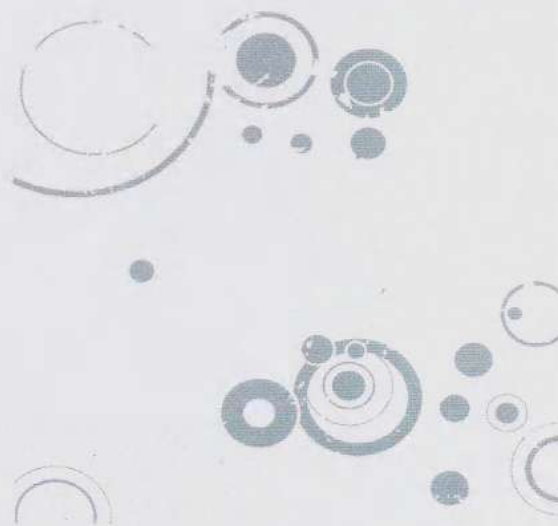
- readily dissolve the substance to be purified at high temperatures, but hardly at low temperatures
- dissolve impurities readily at a low temperature or not at all
- have a relatively low boiling point to be easily evaporated from the purified substance
- not react with the substance to be purified

Solvents may be tested by placing a small amount of the substance to be purified in each of several test tubes and adding a small amount of a different solvent to each. Solubility is noted in the hot and cold solvent.



MIXED SOLVENT

If no single solvent is found suitable, then a mixed solvent can be used. **Mixed solvent** recrystallization requires two miscible solvents. The substance to be purified should be relatively soluble in one solvent and relatively insoluble in the other solvent. For example, a substance which is relatively soluble in ethanol and almost insoluble in water may crystallize well from a mixed solvent. The procedure is to dissolve the solid in a minimum amount of hot ethanol. Insoluble impurities are removed by filtering the hot ethanol. Warm water is added dropwise to produce a precipitate which clears on mixing. When the solution just fails to clear on mixing, a few drops of ethanol are added. The mixture is re-heated then allowed to cool for crystallization.





Questions

1. Describe the steps involved in the purification of a solid by recrystallization.
2. A solution is prepared by dissolving 120 g of potassium nitrate in 200 cm³ of water at 60°C. Calculate the mass of potassium nitrate that will recrystallize from the solution when it is cooled to 30°C given that the concentration of a saturated solution at 30°C is 20 g of potassium nitrate per 100 cm³ of solution.
3. Identify the characteristics of a solvent for effective recrystallization.
4. Explain how a mixed solvent is used in recrystallization.



Gravimetric analysis is based on the measurement of the weight of an analyte or of a compound of known composition that contains the analyte. There are two general types of gravimetric methods. These are **precipitation** and **volatilization**.



PRECIPITATION

Gravimetric analysis of a substance by precipitation involves isolation of an ion in solution as a sparingly soluble precipitate that either has a known composition or can be converted to a product of known composition. The precipitate is filtered and washed free of contaminants, dried or ignited and weighed. The amount of the original ion can be determined from the mass and known composition of the precipitate.

For successful determinations, the precipitate must

- have a sufficiently low solubility so that losses from dissolving are negligible.
- be of known composition after drying or igniting
- be easily filtered
- be readily washed free of impurities
- not react in the atmosphere
- have a high purity. It is difficult to obtain a product which is pure, but careful precipitation and sufficient washing helps reduce the level of impurity.

Unwanted precipitation may occur with the desired product. This is called coprecipitation. It cannot be avoided but can be minimized by slow precipitation and thorough washing. The precipitate should consist of crystals large enough to be easily washed and filtered. Large crystals also have smaller surface areas for surface adsorption of foreign material.

Vacuum filtration

Vacuum filtration is used to increase the filtration rate. The apparatus for vacuum filtration is shown in Figure 32.1. A **Buchner or suction funnel** is fitted to a **suction flask** with an adaptor. A sheet of filter paper of a suitable size just to cover all



Fig 32.1(a)

Apparatus for vacuum filtration



Fig. 32.1 (b)

A Buchner funnel

the holes in the funnel is placed in the funnel and moistened with a little of the solvent to be used in the filtration. The filter flask is then connected to a vacuum source. The mixture to be filtered is poured onto the filter paper and the vacuum rapidly pulls the liquid through the funnel. If the vacuum source is a water aspirator, it is important not to turn off the aspirator or to decrease the aspirator flow rate during filtration as this may cause water to be sucked from the aspirator into the filtration flask. For this reason, it is also important to disconnect the vacuum at the flask before turning off the aspirator. The filtrate is collected in the suction flask. The suction flask is made of thick glass to prevent breakage when a vacuum is applied.

Fig. 32.1

Drying to a constant mass

The filter paper with the product is transferred to a weighed crucible and the filter paper is ignited. For quantitative analysis, **quantitative filter paper** is used. Negligible residue is left on careful ignition of quantitative filter paper. The crucible serves as a container and is selected according to its inertness to the product therefore it does not suffer mass changes nor contaminate the product. **Silica crucibles** have high resistance to heat shock due to its small coefficient of expansion. It can tolerate temperatures higher than 200°C without damage. These are used for heating and igniting small quantities of solids. **Sintered glass crucibles** are porous thus a mixture can be filtered, dry and weighed directly. These have a porous disc of sintered glass fused in the body of the crucible. Sintered glass crucibles are unable to withstand temperatures higher than 200°C .

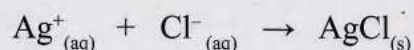
The sample is dried to a constant, reproducible mass. This is especially important in gravimetric analysis because solids may absorb water from the air and increase in weight. The sample is usually dried in a low temperature oven (about 110°C). The oven is electrically heated and can maintain a constant temperature. The sample is allowed to cool to room temperature in a desiccator then weighed. It is heated again, cooled and weighed a second time. The process is repeated until a constant mass is found. It is important to allow the sample to return to room temperature before weighing to prevent convection currents around the balance pan which can lead to a steady increase in mass while the sample is on the pan. This can severely disrupt the accuracy of the method.

Calculation

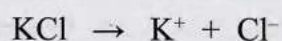
The treatment of a 0.800 g sample of impure potassium chloride with excess aqueous silver nitrate resulted in precipitation of 1.460 g of silver chloride. Calculate the percentage of potassium chloride in the sample.

$$\text{Number of moles in 1.46 g of AgCl} = \frac{1.460}{143.5} = 0.01 \text{ mole}$$

Since 1mole of AgCl is formed from 1 mole of Cl^- ions



and 1mole of Cl^- ions is formed from 1mole of KCl



the number of moles of KCl reacted = 0.01 moles

$$\text{The mass of 0.01 moles of KCl} = 0.01 \times 74.5 = 0.745 \text{ g}$$

$$\text{Thus the \% KCl in the sample} = \frac{0.745}{0.800} = 93.13 \%$$



VOLATILIZATION

Gravimetric analysis of a substance by volatilization involves heating an analyte or its decomposition products into the gaseous form. The gaseous products can be collected and weighed or the mass of the product can be determined indirectly from the loss in mass of the sample.

Volatilization is commonly used to determine the amount of water and carbon dioxide in a sample. For example, the amount of water in a sample can be determined by heating the sample and collecting the water vapour in a solid desiccant. The amount of water can be determined from the increase in mass of the desiccant. Alternatively, the amount of water can also be determined indirectly from the mass loss from the sample as a result of heating. The latter assumes that water is the only component volatilized. However this indirect method is often unjustified as heating of many substances result in their decomposition and consequent change in mass regardless of the presence of water.

Carbon dioxide can be determined from decomposition of carbonates. The mass of carbon dioxide is determined from the increase in weight of a solid absorbent. Ascarite II is an absorbent which consists of sodium hydroxide in a non-fibrous silicate. It



absorbs carbon dioxide by the following reaction



Thus the absorption tube must also contain a desiccant to prevent the loss of water.

Carbon and hydrogen in organic compounds can also be determined by gravimetric methods. Combustion gives carbon dioxide and water which can be collected and weighed.

Example

A 2.5 g sample of impure calcium carbonate was decomposed with excess hydrochloric acid. The liberated carbon dioxide collected in an absorbent was found to weigh 0.88 g. Calculate the percentage of calcium carbonate in the sample.

$$\text{Number of moles in 0.88 g of CO}_2 = \frac{0.88}{44} = 0.02 \text{ mole}$$



1 mole of CO_2 is formed from 1 mole of CaCO_3

therefore 0.02 mole of CaCO_3 was used in the reaction

$$\begin{aligned} \text{mass of CaCO}_3 \text{ used} &= 0.02 \times 100 \\ &= 2 \text{ g} \end{aligned}$$

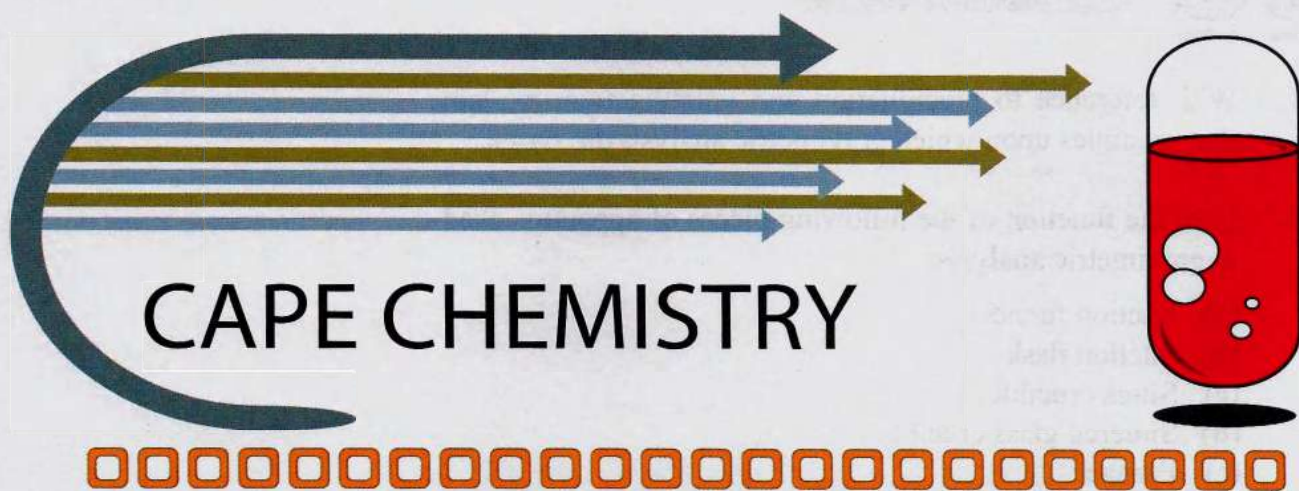
$$\begin{aligned} \% \text{ CaCO}_3 \text{ in sample} &= \frac{2 \times 100}{2.5} \\ &= 80 \% \end{aligned}$$



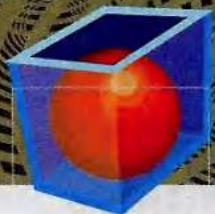
Questions

1. With reference to precipitation and volatilization, explain the principles upon which gravimetric analysis are based.
2. Give the function of the following pieces of apparatus used in gravimetric analysis:
 - (a) Suction funnel
 - (b) Suction flask
 - (c) Silica crucible
 - (d) Sintered glass crucible
 - (e) Furnace
3. The treatment of a 0.500 g sample of impure sodium chloride with excess aqueous silver nitrate resulted in precipitation of 0.860 g of silver chloride. Calculate the percentage of sodium chloride in the sample.
4. A 8.4 g sample of impure copper (II) carbonate was decomposed with excess sulphuric acid. The liberated carbon dioxide collected in an absorbent was found to weigh 2.20 g. Calculate the percentage of copper (II) carbonate in the sample.





SECTION 6
Industry and the Environment



Locating Industrial Plants

The choice of the site for an industry is based on the advantages and disadvantages of the available locations. Factors such as cost of production and distribution, additional space for expansion and safety of the community and the environment must be considered when selecting a site.

Locating a plant as near as possible to the source of raw materials is very important as it reduces the cost of transportation and storage. The supply of raw materials must be cheap and reliable to keep the cost of production at a minimum value.

Large quantities of water are used in the industry for cooling, steam generation and as a raw material. Many industrial plants are located along large rivers or lakes where the supply of water is available and reliable. In areas where the water supply may fluctuate, reservoirs may be built. A cheap supply of water is needed to minimize cost of production.

Since energy requirements are generally high in the industry, the plant is usually located near a cheap source of energy for economical production. Consideration is also given to the availability of appropriately skilled labour in the vicinity of a proposed plant site.

Transportation links and the proximity to major markets are also taken into consideration as these reduce the cost of distribution of products and the time required for shipping. Plants are usually located near to ports for easy import and export of materials.

It may become necessary to expand the facilities of a plant in the future therefore a site where additional space is available is important even though no immediate expansion is planned.

The safety of the workers and the people who live in the surrounding areas is very important when selecting a site for a plant. All potential risks must be minimized therefore the site should have the capacity to facilitate treatment and disposal of waste in a proper manner so as to control pollution in the environment. Consideration is thus given to the legal restrictions, building codes and permits required for the location of a plant in a particular area.





SAFETY REQUIREMENTS FOR THE INDUSTRY

The industrial environment may impact on lives of workers as well as nearby communities. Unsafe working conditions and practices may result in injuries, diseases and even death of people. Identifying and controlling hazards in the industry can save lives and money as well as improve productivity. Some general safety requirements in the industry are as follows:

- The industry should have an emergency action plan for workers to ensure their safety in case of an accident, a fire or other emergencies.
- Workers should be aware of emergency exit routes in the workplace.
- Safety standards for floors, aisles, platforms, ladders, stairways, and other walking or working surfaces should be followed to prevent accidents such as slips, trips, and falls.
- Medical and first aid personnel and supplies should be available to deal with the particular hazards of the workplace.
- Workers should know about hazards in the workplace and how to use safety equipment to protect themselves.



Safety equipment used to protect workers.

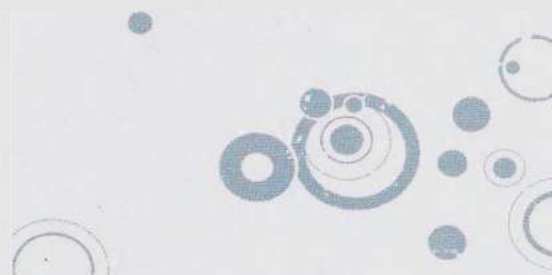
Health and safety is very important in the daily running of any industry. Many accidents can be avoided by being cautious, wearing and using safety equipment, and following safe practices.





Questions

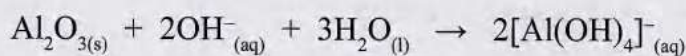
- List three factors that are taken into consideration for the choice of a site for an industry.
 - The safety of the people who live in the surrounding areas of an industry is very important when selecting a site for a plant. Discuss how potential risks can be minimized in surrounding areas.
- What is the significance of locating a plant close to the following areas:
 - a source of raw materials
 - along a river
 - cheap source of energy
- List three safety requirements in an industry.
 - Discuss two ways by which accidents can be avoided in the industry.
 - Why should workers know about the hazards in the industry where they are employed?





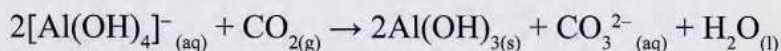
EXTRACTION OF ALUMINIUM

Aluminium is extracted commercially by electrolysis of molten aluminium oxide. This is obtained from bauxite which is its most common ore and contains about 50 % aluminium oxide (alumina). The main impurities in the ore are iron (III) oxide and silicon (IV) oxide. Pure aluminium oxide is obtained by removing its impurities from bauxite. This is done by making use of the fact that aluminium oxide is amphoteric whereas iron (III) oxide is basic and silicon (IV) oxide is acidic in nature. The ground bauxite is heated with concentrated sodium hydroxide solution which dissolves the aluminium oxide and silicon (IV) oxide.

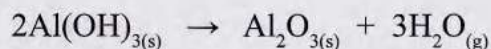


The iron (III) oxide and other basic materials remain undissolved and are removed by filtration. The residue which is highly alkaline and red-brown in colour due to the presence of the iron (III) oxide is called 'red mud'. This poses major environmental problems to dispose.

The filtered solution is then seeded with solid aluminium hydroxide or carbon dioxide is blown through the solution to precipitate aluminium hydroxide. The silicate ions remain dissolved in solution.



The aluminium hydroxide is filtered, washed and heated to form pure alumina, Al_2O_3 .



The aluminium oxide is then electrolysed to obtain aluminium. This process is referred to as **smelting**. Electrolysis is done using molten solids since aluminium is very reactive and not preferentially discharged in aqueous solution. Unfortunately, alumina has a high melting point (2050°C) and it is not practical to do electrolysis at such a high temperature. However in 1886



Hall and Heroult independently discovered that the melting point of alumina was significantly reduced when dissolved in cryolite (Na_3AlF_6) and fluorspar (CaF_2). Thus alumina is electrolysed in molten cryolite and fluorspar with a voltage of about 5 volts and a current of about 100,000 amperes. This maintains the cell or 'pot' at about 950°C . The cell consists of a steel container lined with graphite which acts as the cathode, the molten electrolyte and graphite anodes suspended in the electrolyte (fig. 34.1).

Fig. 34.1

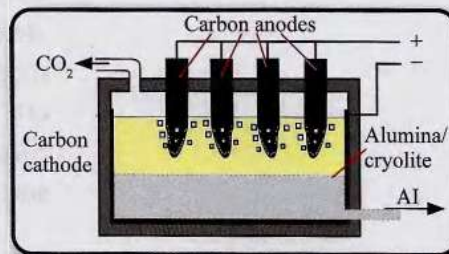
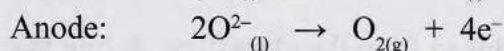
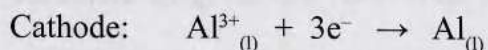


Fig. 34.1

The reactions that take place in the electrolyte are complex, but the overall electrode reactions result in aluminium being discharged at the cathode and oxygen given off at the anode.



Aluminium does not mix with the electrolyte and falls to the bottom of the cell where it can be tapped off as a pure liquid metal. At the temperature of the cell, the carbon anodes burn in oxygen to form carbon monoxide and carbon dioxide gases and must be replaced continually.

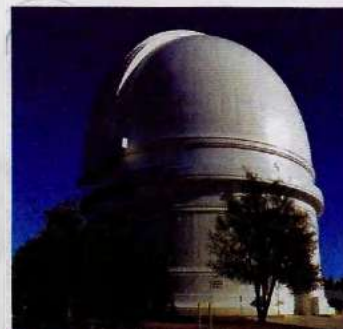


USES OF ALUMINIUM

Aluminium was once considered a precious metal and only used for decorative items. However after electrolytic reduction was discovered, aluminium was no longer expensive and found widespread use.

The range of uses for aluminium reflects its properties. Aluminium is used to make cooking utensils as it is a good thermal conductor. It also acts as a thermal insulator as it is a good reflector of radiant heat and light. This makes it useful in coating firefighters' garments which can reflect heat from the fire to keep the firefighter cool. This insulating property is sometimes utilized in hospitals whereby premature babies are wrapped in aluminium foil to keep them warm. Since its polished surface is highly reflective and more durable than silver, it is also used as mirrors. Large reflecting telescopes such as the Hale 200 inch telescope have aluminium mirrors.

Its low density and resistance to corrosion make aluminium foil ideal for packaging food products. It is also used for making small



The 200 inch Hale telescope is located at the Palomar Observatory in California.



containers such as soft drink cans. These can be easily opened with pull tabs that tear the metal along scored lines. Aluminium is strong when alloyed with other elements such as silicon, copper or magnesium. It has significant usage where strong, light materials are required such as in the construction of aircrafts and rockets. Since aluminium is light and a good conductor of electricity, it is suitable for making electrical transmission lines.



IMPACT OF THE ALUMINIUM INDUSTRY

Approximately one tonne of red mud residue must be disposed for each tonne of aluminium oxide produced. The caustic residue can percolate into the underground water of local areas. This can significantly increase the sodium concentration and pH of the water. Sodium is known to be associated with a higher incidence of hypertension.

Fluoride gases are also produced from the electrolyte during the process. Although about 98 % of these gases are scrubbed out and recycled, the 2 % that escape into the atmosphere slowly accumulate in the environment and can cause damage to plants many kilometres away. Fluorides can also enter the food chain as livestock graze on grass exposed to it. The symptoms of fluoride damage in animals and humans include dental mottling, stiffness in knees and joints, anaemia and respiratory distress.

The economical disposal of used carbon cell linings remains a problem. The linings contain highly alkaline bath, aluminum carbide, cyanides, and other materials. A small part is ground and added to cement kilns as a source of fluoride, but most still end up in landfills. Exposure to coal tar pitch volatiles from the carbon electrodes and cryolite are associated with increased risk of bladder and lung cancer.

Aluminium smelting requires an enormous amount of electricity since 3 moles of electrons are needed to discharge 1 mole of aluminium. A modern smelter pot is typically 10 metres long, 4 metres wide and 1.5 metres high and takes about 15 000 kilowatt hours of electricity to produce about 1 tonne of aluminium per day. There are about 100 of these pots in a room, thus the cost of electricity is central to the economics of the process. Smelting generally takes place in areas where electricity is cheap and abundant. This is usually done in places where hydroelectric power is available. Pollution caused by power generation depends on how the electricity is generated.



a red mud pond





Questions

1. In the production of aluminium, the overall chemical change that occurs can be represented by the equation below.



Give details of the various stages of the extraction process of aluminium. Write equations for the relevant reactions occurring in the extraction process and explain how the above equation is an overall simplification.

2. (a) Aluminium is extracted from bauxite in an electrochemical process. Draw a labelled diagram to illustrate the extraction of aluminium from bauxite.
- (b) What are the main reasons for mixing cryolite to the bauxite mixture?
- (c) Explain why the anode must be periodically replaced.
- (d) Write equations for the reactions occurring at the cathode and anode of the electrolytic cell and name the products formed at each electrode.
3. Aluminium is widely used in the home and industry. It is used to manufacture pots and pans, to wrap premature babies, as a coating for suits of firefighters as well as in car headlights.
- (a) Justify the uses of aluminium mentioned above by referring to the properties of aluminium.
- (b) Aluminium smelting is considered dangerous to the environment. Discuss this statement.



Crude oil is a complex mixture of naturally occurring hydrocarbons found within the earth. It was formed from the remains of microscopic plants and animals that were buried and preserved in rocks millions of years ago. These remains slowly decayed as they were buried deeper within layers of rocks and with time and temperature they were converted to crude oil. Similar conditions have also led to the formation of natural gas which is frequently found associated with crude oil. Together crude oil and natural gas is referred to as petroleum (Greek for “rock oil”).

Crude oil consists mainly of a variety of alkanes, cycloalkanes and aromatic hydrocarbons. There are also small amounts of other substances such as compounds of nitrogen, oxygen and sulphur. Crude oil from different areas of the world or even different depths in the same oilfield varies slightly. Thus the composition and appearance of crude oil depend on its source. Most crude oil looks like a thin, brown treacle, while some are almost colourless volatile liquids and others are thick black oils.



Petrotrin oil refinery in Trinidad and Tobago.

The uses of crude oil as it comes from the ground are limited. However maximum value can be obtained from this natural resource when it is used as a raw material. Crude oil must be separated into its various components and selectively modified before it can be useful. This process is called refining and occurs in an oil refinery. Once the crude oil is extracted and transported to the oil refinery, it is transformed into fuel for transportation and electric power generation as well as feedstock for the petrochemical industry. The primary process for separating the components of crude oil is fractional distillation.



FRACTIONAL DISTILLATION OF CRUDE OIL

The components of crude oil have different boiling points due to the arrangement and variation in the number of carbon atoms in the hydrocarbon molecules. Fractional distillation uses this difference in boiling point to separate these components.

The crude oil is heated to about 400°C and passed into a fractionating column which may be as high as 60 metres. The column consists of a number of horizontal trays at intervals along



its height. It is heated at the base but the temperature gradually decreases towards the top of the column thus each tray is slightly cooler than the one below it.

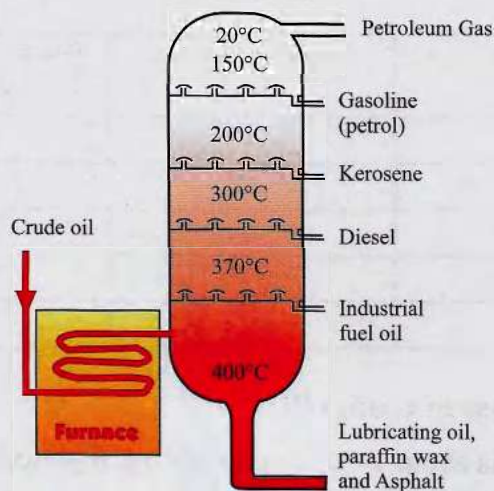


Fig. 35.1 Fractional distillation of crude oil

The vapour rises up the column and condenses on a tray where the temperature is lower than its boiling point. The trays have holes in them which are covered by bubble caps. As more rising vapour passes through the holes in the tray, the bubble caps direct the vapour through the liquid already on the tray. This causes the lighter components condensed in the tray to vaporize again and continue to move up the column.

There are also overflow tubes at the side of the trays which allow liquid to flow back down the column. When this liquid reaches a lower tray, the higher temperature there brings about vaporization of the more volatile component which then rises up the column.

As the vapour condenses and vaporizes many times on the trays along the column, the composition of the vapour becomes richer in the more volatile component (i.e. the one with the lower boiling point). The more volatile components rise to the top of the column while the less volatile ones tend to condense on the trays at various levels along the column. Thus the crude oil is separated into different fractions, each boiling within a particular temperature range.

The different fractions are drawn off at various levels along the column. The lightest fraction comes off at the top of the column as a gas. It contains fewer carbon atoms and has the lowest boiling point range. As you go down the column, the fractions become heavier and have a higher boiling point range. The typical



fractions of crude oil and their boiling point ranges are shown in Table 35.1 below.

Table 35.1

Fraction	Length of carbon chain	Boiling temperature range /°C
Refinery gas	$C_1 - C_4$	< 20
Gasoline & naphtha	$C_5 - C_{10}$	40 – 200
Kerosene	$C_{11} - C_{18}$	175 – 325
Gas oil (diesel oil)	$C_{18} - C_{25}$	275 – 350
Residue	> C_{25}	> 350

Major fractions of crude oil

Refinery gas is about 1 – 2 % of crude oil. It is mainly a mixture of alkanes containing up to four carbon atoms in a molecule and is usually a gas at room temperature. Refinery gas can be used as a gaseous fuel or it can be liquefied under pressure to produce liquefied petroleum gas (LPG). It can also be used as feedstock for making petrochemicals.

Gasoline & naphtha are about 15 – 30% of crude oil. Gasoline is distilled off and used as motor fuel for internal combustion engines. The other part, naphtha, is used as chemical feedstock for conversion to other compounds.

Kerosene is about 10 – 15% of crude oil. It is used as jet fuel and for domestic heating. It can also be broken down to produce more gasoline.

Gas oil (diesel oil) is about 15 – 20% of crude oil. It is used as a fuel in diesel engines and industrial furnaces.

Residue is about 40 – 50% of crude oil. It can be further distilled under low pressure to yield fuel oil, lubricating oil, waxes and bitumen. Reducing the pressure lowers the boiling point and allows the heavier components to be separated without breaking down. **Fuel oil** is used as fuel for ships and power stations. **Lubricating oils and waxes** are used for motor oil, grease and other lubricants. **Bitumen** is used for road surfacing and roofing material.



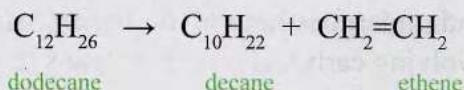


CRACKING AND REFORMING OF CRUDE OIL FRACTIONS

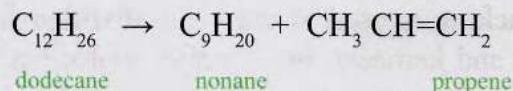
Although there are uses for the various fractions of crude oil, the demand for the lighter fractions such as gasoline is greater than the amount supplied by fractional distillation. To satisfy this demand, oil refineries convert the less used heavier fractions into more valuable ones. Two important processes used for this purpose are **cracking** and **reforming**.

Cracking

Cracking is a process in which large hydrocarbon molecules are broken down into smaller molecules. The cracked products may be smaller alkanes, alkenes and hydrogen molecules. The large hydrocarbon molecule can break anywhere along the carbon chain to form a variety of smaller molecules. For example, dodecane can break into decane and ethene



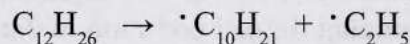
or nonane and propene.



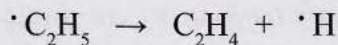
Cracking is carried out either using heat (**thermal cracking**) or a catalyst (**catalytic cracking**).

Thermal cracking

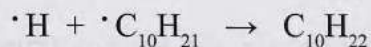
Thermal cracking involves rapidly heating the hydrocarbon to temperatures of about 800°C and then cooling it. This process occurs within a second. The high temperatures can cause the C – C bond to undergo homolytic fission. This results in the formation of free radicals. For example, dodecane can form a decyl radical and an ethyl radical.



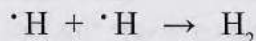
These free radicals can then undergo further reactions. The ethyl radical can lose a hydrogen atom to form ethene.



The hydrogen atom, which is a free radical, can combine with the decyl radical to form decane



or two hydrogen atoms can combine to form hydrogen gas.



Since the carbon chain can split in a number of ways, a wide variety of smaller molecules are produced which can be separated by fractional distillation. Thermal cracking is generally used for cracking the **residue fraction** of crude oil.

Catalytic cracking

Catalytic cracking (cat-cracking) involves the use of a catalyst at lower temperatures to break the bonds of the hydrocarbon molecules. The reaction is usually catalyzed by a powdered mixture of alumina and silica ($\text{Al}_2\text{O}_3/\text{SiO}_2$) at about 500°C . The C – C bond undergoes heterolytic fission which results in a mechanism involving carbocations. This tends to produce a large amount of branched chain alkanes which are useful in gasoline. Branched chain alkanes give gasoline a higher octane number.

Catalytic cracking is used to crack the **distilled fractions** such as diesel oil and kerosene into smaller molecules. The cracked compounds are important to produce more valuable fuel as well as chemical feedstock for the petrochemical industry. The alkenes are suitable starting materials to make plastics, detergents, cosmetics, solvents, paint and many other petrochemicals.

Octane number of gasoline

When the gasoline-air mixture is compressed in the internal combustion engine, some hydrocarbons ignite spontaneously without a spark and explode prematurely to cause a '**knocking**' noise. Knocking can damage the engine and reduce the efficiency of the gasoline. **Tetraethyl lead** was once added to gasoline as an anti-knock agent. However the leaded gas is known to cause an unacceptable amount of lead pollution in the environment. In most countries, leaded fuel has been largely replaced by unleaded fuel which contains more branched chain alkanes. Branched chain alkanes ignite less spontaneously than straight chain isomers therefore they are more resistant to knocking. The anti-knocking properties of gasoline are measured on an octane scale using 2,2,4-trimethylpentane and heptane. 2,2,4-Trimethylpentane has a low tendency to ignite spontaneously when compressed and



A cat cracker converts more of each barrel of oil into gasoline.



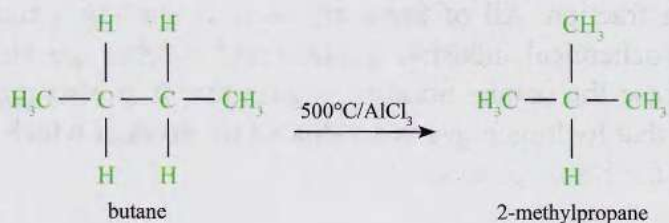
is given an octane number of 100. Heptane knocks readily with little compression and is given an octane number of 0. A blend of gasoline is assigned an octane number by comparing it with different mixtures of 2,2,4-trimethylpentane and heptane.

Reforming

Reforming is a process which converts straight chain hydrocarbons into aromatic and more highly branched hydrocarbons. This process converts low value naphtha fractions into high grade gasoline components. Higher grade gasoline contains a higher proportion of branched alkanes and aromatic hydrocarbons. Products of reforming are also used as starting materials in the petrochemical industry. Reforming is the effect of numerous reactions such as **isomerization**, **alkylation** and **catalytic reforming**.

Isomerization

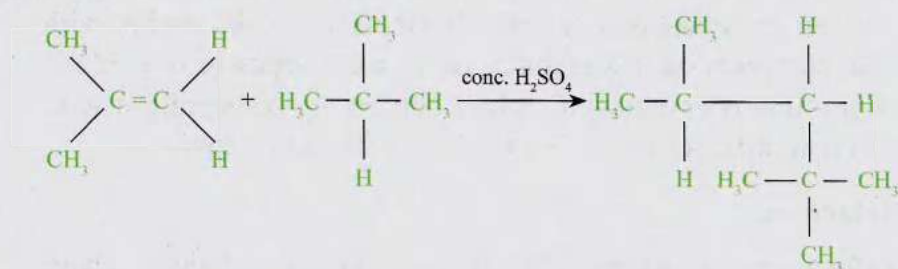
This involves breaking up straight chain hydrocarbons and reassembling them as branched chain isomers. The reaction takes place at about 500°C in the presence of an aluminium chloride catalyst. Isomerization is important for the conversion of normal pentanes and hexanes into higher branched isomers for gasoline blending. It is also used to convert butane into 2-methylpropane to provide additional feedstock for alkylation units.



Alkylation

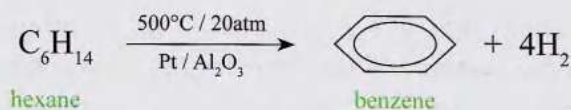
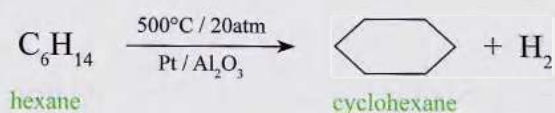
In this process tertiary alkanes combine with alkenes to make longer branched chain alkanes. The product is a blend of alkanes with high octane numbers. The reaction occurs at room temperature and is catalyzed by concentrated sulphuric acid. For example, 2-methylpropane is added to 2-methylpropene to form 2,2,4-trimethylpentane which has exceptional anti-knock properties.





Catalytic reforming

This process converts straight chain alkane molecules of the naphtha fraction into cycloalkanes and aromatic hydrocarbons. The naphtha vapour is heated to about 500°C at a pressure of 20 atm and then passed over a catalyst made of platinum and aluminium oxide. The equations for the conversion of hexane to cyclohexane and hexane to benzene are given below.



Benzene, toluene and the xylenes are some of the main aromatic products of reforming the $\text{C}_6 - \text{C}_8$ hydrocarbons from the naphtha fraction. All of these are used as starting materials in the petrochemical industry. Toluene and xylenes are also used to increase the octane number in gasoline. It is also important to note that hydrogen gas is a valuable by-product which can be used in the Haber process.



IMPACT OF THE OIL INDUSTRY ON THE ENVIRONMENT

The oil industry is considered a major source of pollution to the environment. Pollution may occur during extraction, transportation and refining of the crude oil. Also the use of its refined products has an impact on the environment.

Extraction of crude oil involves emissions of pollutants from the first seismic survey until the field is shut down. Well drilling discharges oil into surrounding soil and water. This can damage fragile ecosystems by destroying habitats and killing organisms.

Oil is usually transported through pipelines and in large ocean tankers. This presents the possibility of accidental leaks and spills.

In 1979 the Atlantic Empress spilled 42.7 million gallons of oil as the result of a collision with the Aegean Captain in the Caribbean Sea near Trinidad and Tobago. Oil spills are detrimental as organisms are at risk of inhaling or ingestion the oil which can poison them. When sea birds are covered with oil, their feathers stick together and they lose their ability to fly. The oil also sticks down the fur of animals (e.g. polar bears) which causes them to lose insulation and freeze to death. Oil spills also ruin coral reefs and beaches thereby affecting the tourism industry.



Collision between the Atlantic Empress and Aegean Captain started a fire that burned for 15 days.

There are several different methods for dealing with oil spills on the surface of the water. Some of these are given below.

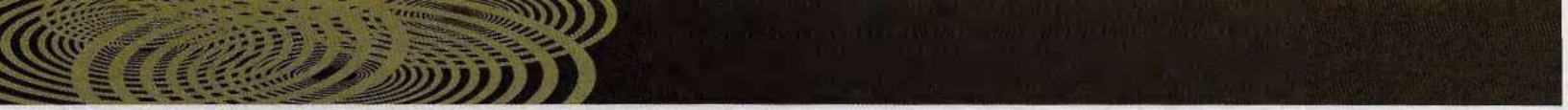
- A floating barrier called a boom is placed around the oil to keep it from spreading.
- The oil can be ignited within the boom.
- A giant vacuum can be used to suck up the surface oil.
- Absorbents are used to collect the oil left behind from suctioning. Natural absorbents like clay and sand can hold up to 20 times their weight in oil while synthetic absorbents like polyethylene can hold up to 70 times its weight in oil.
- Solvent compounds are used to break down light oil spills and disperse it.
- Natural bacteria that use the petroleum products as food are often effective at cleaning up oil spills although they may take years to work.

In the refining process, hazardous and toxic air pollutants such as carbon monoxide, hydrogen sulphide, nitrogen oxides, sulphur dioxide and BTEX compounds (benzene, toluene, ethylbenzene, and xylene) are emitted into the atmosphere. There are concerns about the effects of exposure to these chemicals.

Carbon monoxide is toxic because it combines readily with haemoglobin in the blood to form the stable compound carboxyhaemoglobin. This makes the haemoglobin unable to transport oxygen which results in the cells of the body being deprived of oxygen. A concentration as little as 400 ppm in the air can be fatal.

Sulphur dioxide and nitrogen oxides contribute to the formation of acid rain. The effects of acid rain include erosion of stonework on buildings, destruction of trees and acidifying lakes which results in the death of fish.





BTEX compounds are possible carcinogens and may cause reproductive and developmental problems. They may also aggravate respiratory conditions such as asthma.

Wastewater in refineries may be contaminated with oil residues and other hazardous wastes from equipment leaks and spills. Although this water is treated before being released into the environment, some of these wastes may end up in aquifers and groundwater.

Most of the petroleum in the world is used as fuel for transportation and electric power generation. This releases large amounts of carbon dioxide, a greenhouse gas, which contributes to global warming. The use of hydrocarbon fuels in vehicle engines also release other gases such as nitrogen oxides which contribute to acid rain and toxic carbon monoxide. The part of petroleum that is used as feedstock for the petrochemical industry is utilized in making thousands of products. These include plastics, fertilizers, detergents and cosmetics, all of which eventually end up in the environment. Products like plastics are difficult to dispose of as they are not readily degradable and they release toxic fumes when burnt.



Questions

1. The major product extracted from the earth by the petrochemical industry is crude oil. The crude oil undergoes many stages of refining to produce a large number of products.
 - (a) What do you understand by the term *petrochemical refining*?
 - (b) Identify three benefits that are obtained from petrochemical refining.
 - (c) Rigid environmental regulations have recently been imposed on the petrochemical industry. Discuss this statement.
2.
 - (a) Explain the principles involved in fractional distillation.
 - (b) Why is fractional distillation of crude oil important?
3.
 - (a) What do you understand by the term *cracking*?
 - (b) What is the significance of cracking larger fractions of crude oil?
 - (c) Write a balanced equation to illustrate cracking.
4.
 - (a) State three adverse effects associated with the extraction of crude oil and comment on the environmental problems that result.
 - (b) Explain how the refining process can contribute to acid rain.
 - (c) Give two sources of hydrocarbons in the atmosphere.
5. Since there are environmental dangers associated with the use of leaded petrol, there is increase use of unleaded petrol.
 - (i) Comment on the dangers associated with the use of leaded petrol.
 - (ii) Account for the presence of carbon monoxide and nitrogen oxides in the exhaust fumes of vehicles.
 - (iii) Suggest how gases such as carbon monoxide and nitrogen oxides present in exhaust fumes can be minimized.





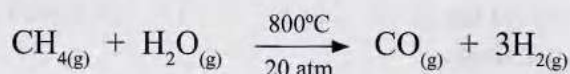
THE HABER PROCESS

The Haber process is a method used to make ammonia directly from nitrogen and hydrogen. It was developed by the German chemist, Fritz Haber, for which he received the Nobel Prize for Chemistry in 1918. This process was transformed into large scale production using high pressure methods developed by Carl Bosch who was awarded the Nobel Prize in 1931 together with Friedrich Bergius for high-pressure studies.

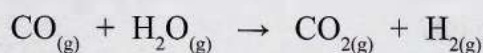


Ammonia production facility located in central Trinidad. Ninety-nine percent of the annual production is exported. This makes Trinidad and Tobago the world's leading exporter of ammonia.

The nitrogen is obtained from fractional distillation of liquefied air while the hydrogen is derived mainly from natural gas and water in steam reforming.



The carbon monoxide produced is combined with more steam to form hydrogen and carbon dioxide.



The combination of nitrogen and hydrogen into ammonia is a reversible reaction. The forward reaction is exothermic and results in a decrease in volume.

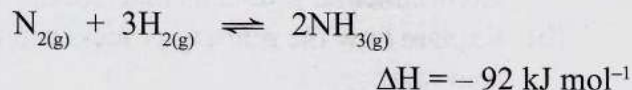
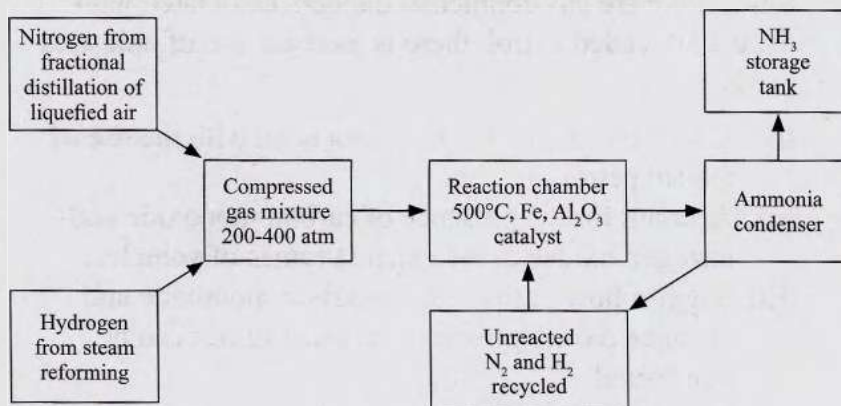


Fig. 36.1 A flow diagram of the Haber process.



According to Le Chatelier's Principle, since the reaction is exothermic and results in a decrease in volume i.e. four moles of reactants form two moles of products, low temperature and high pressure would shift the equilibrium to the right and increase the yield of ammonia. Thus the forward reaction will be favoured by low temperature and high pressure. However, at low temperatures, the reaction rate would be too slow to be economical and at very high pressures the cost and maintenance of equipment would be very expensive.

For commercial production a compromised temperature of about 450°C is used with a catalyst. This produces a yield of about 10% ammonia at an acceptable reaction rate. The manufacturer wants to produce as much ammonia as possible per day therefore it is more economical to produce a lower yield of ammonia in a short time rather than wait several years for the equilibrium mixture to reach a very high yield.

The catalyst is usually iron mixed with small amounts of promoters such as potassium oxide and aluminium oxide. The catalyst has no effect on the position of the equilibrium. It only lowers the activation energy and hence increases the rate of the reaction at lower operating temperatures. The promoters increase the efficiency of the catalyst. Purification of both the nitrogen and hydrogen gases is necessary to prevent 'poisoning' of the catalyst.

Increase pressure increases the yield of ammonia and the rate of the reaction. Therefore the only compromise in pressure is the economical consideration. For commercial production, the reaction is usually carried out at pressures ranging from about 200 to 400 atmospheres. The cost of producing ammonia at very high pressure is very expensive and may not be worth the further increase in yield of ammonia.

Separating the ammonia

As the equilibrium mixture of gases leaves the reactor, the temperature of the mixture is lowered enough for the ammonia to turn into a liquid while the nitrogen and hydrogen remain as gases. The liquefied ammonia is removed from the system while the unreacted nitrogen and hydrogen gases are recycled. The ammonia is removed from the system as soon as it is formed to maintain the position of equilibrium to the right. About 10% ammonia is produced per cycle however a yield of about 98% is obtained by recycling the gases.





Application of anhydrous ammonia to soil at low temperatures



USES OF AMMONIA

A large amount of the ammonia produced is used in the agriculture and fertilizer industry. Ammonia can be applied to soil directly as liquid ammonia or it can be used to produce fertilizers such as urea, ammonium and nitrate salts. Nitrogenous fertilizers provide a valuable source of nitrogen which is necessary for healthy plant growth. Ammonia and urea are also used in livestock feeds as a source of protein.

In the chemical industry ammonia is used to manufacture nitric acid which is used to make explosives. Other uses of ammonia include the manufacture of sodium carbonate, pharmaceuticals, plastics, paper and textiles. Industrial refrigeration systems also use ammonia as a refrigerant because it is easily liquefied by compression or cooling and absorbs a large amount of heat from its surroundings. Ammonia solutions are also widely used as commercial and household cleaners.



IMPACT OF THE AMMONIA INDUSTRY ON THE ENVIRONMENT

Emission of gases from the ammonia industry is minimized by recycling unreacted nitrogen and hydrogen. Most of the carbon dioxide produced in the steam reforming process can be utilized in urea production. It must be noted however, that the majority of ammonia emitted into the environment does not come from the Haber process itself, but from the various industries which uses ammonia. A large amount of ammonia emitted is generated from the fertilizer and agriculture industry.

Ammonia is used in the fertilizer and agriculture industry to increase food production. As a result, a large amount of ammonia and nitrogenous compounds end up in the environment. Exposure to ammonia can cause severe irritation at low concentrations and can be fatal at high concentrations. Precautions have to be taken to reduce possible hazards when storing and handling ammonia. Ammonium and nitrate fertilizers are water soluble and are easily washed out from farmlands into the waterways. Excess fertilizers in rivers and streams cause **eutrophication**. This is a process whereby the excess nutrients in the water stimulate rapid plant growth on the surface of the water. This enhanced plant growth, often called algal bloom, prevents light from reaching plants lower in the water. These plants die and bacteria use up the dissolved oxygen in the water for decomposition. This results



in the death of fish and other aquatic animals which relies on oxygen for respiration.



Enhanced plant growth in a pond

Since groundwater and surface water are used as sources of domestic water supply, fertilizers can pollute drinking water. Too much nitrates in drinking water is poisonous to infants. The nitrates are converted to nitrites in infants which combine with haemoglobin more readily than oxygen. This starves the body of oxygen and results in a bluish skin discolouration. This condition is called methaemoglobinaemia or “blue baby” syndrome. The ability to metabolize nitrate is developed as children get older hence reducing the occurrence of this problem with age. Nitrates are also classified as being potentially carcinogenic in humans as nitrites derived from nitrates may react with amines in the diet to form carcinogenic compounds. The maximum concentration of nitrate in drinking water which is considered to be safe is 10 ppm.



NaNO_3 and NaNO_2 are used in the curing and preserving of meats.





Questions

1. Ammonia is produced industrially via the Haber process.
 - (a) Write an equation to represent the production of ammonia.
 - (b) State the raw materials and conditions used in the Haber process.
 - (c) Why is the temperature used in the Haber process often described as a compromise?
 - (d) State two uses of ammonia.
2. Ammonia is produced by combining nitrogen and hydrogen.
 - (a) Identify the source of nitrogen used in the process.
 - (b) Hydrogen is obtained by reacting methane with water. Write a balanced equation for this reaction. What condition is required to yield hydrogen?
 - (c) Identify the conditions used in the industrial production of ammonia.
 - (d) Ammonia is stored in storage cylinders. Under what conditions is the ammonia stored in the cylinders.
3.
 - (a) Describe the Haber process for the manufacture of ammonia. Your answer should include the conditions and an equation for the reaction.
 - (b) Le Chatelier's principle suggests that an increase in pressure and a decrease in temperature will increase the yield of ammonia at equilibrium. Justify the choice of conditions for the Haber process as stated.



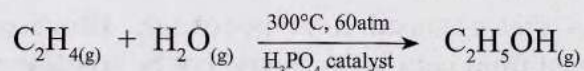


MANUFACTURE OF ETHANOL

There are two major industrial ways to manufacture ethanol. One method is the catalytic hydration of ethene and the other is fermentation of sugars with yeast.

Hydration of ethene

Ethanol is produced by the catalytic hydration of ethene. Ethene and steam are passed over a phosphoric acid catalyst at 300°C and 60 atm.



Ethanol produced by this method is used mainly in the industry as a solvent and in the manufacture of a wide range of pharmaceutical products.

Fermentation

Alcoholic drinks are produced by fermentation of sugars in fruit juices. This is brought about by a group of enzymes present in yeast, a unicellular fungus. Yeast secretes the enzyme invertase which catalyzes the conversion of sucrose to glucose and fructose. These simple sugars are then converted to carbon dioxide and ethanol by another enzyme, zymase, which is also produced by the yeast.



At 25°C the fermentation process takes about three days. The process stops naturally as the yeast dies when the alcohol exceeds its tolerance level. Yeast can tolerate alcohol concentration up to about 20% depending on the yeast strain. Distillation is used to make beverages with higher alcohol content.

Fractional distillation

The fermented mixture is concentrated by fractional distillation. This involves successive vaporization and condensation of the mixture along a fractionating column. As the vapour rises up the



Alcoholic beverages



column, it becomes richer in the more volatile component of the liquid from which it distils.

A mixture of ethanol and water cannot be separated completely by distillation because it forms an **azeotropic mixture** with a minimum boiling point. The boiling point of ethanol is 78.3°C and that of water is 100°C while the azeotrope which contains 95% ethanol and 5% water boils at 78.15°C .

In distillation, the most volatile component (i.e. the one with the lowest boiling point) distills off first. In this case, the azeotrope which contains 95% ethanol and 5% water has the lowest boiling point and distills off first. So no matter how efficient the fractionating column is, 95% alcohol cannot be further concentrated by distillation.

When ethanol is obtained from fermentation it is known as **bioethanol**. There is no chemical difference between fermented ethanol and that obtained from petroleum. However, ethanol that is derived from petroleum should not be considered safe for consumption as it contains about 5% methanol and may cause blindness or death.



USES OF ETHANOL

Ethanol is widely used as a solvent in the pharmaceutical and cosmetic industry. It has a low toxicity and is able to dissolve non-polar substances. This makes it useful as a solvent in medical drugs and perfumes. Ethanol is often used as an antiseptic, to disinfect the skin before injections are given. Ethanol based soaps are now becoming popular in restaurants and are particularly convenient due to its volatility and its antiseptic properties.

The growing demands for gasoline and environmental concerns have led to increased interest in ethanol as a fuel. Ethanol is extensively used as a fuel additive but the use of ethanol alone as a fuel or as part of a mix with gasoline is not as common. Ethanol is mixed with gasoline as an octane enhancer since its octane rating is higher than ordinary gasoline. Ethanol burns more cleanly than gasoline or diesel since ethanol molecules contain oxygen which brings about more complete combustion. Thus carbon monoxide emissions can be 80-90% lower when ethanol is burnt compared to gasoline. However, ethanol has 37% less energy per litre than gasoline. It is also degrading to some plastic and rubber parts of engines designed to use gasoline. Thus corrosion-resistant



Millions of people today operate their vehicles with E85 ethanol, a blend of 85% ethanol and 15% gasoline.



materials and engine modification are required to overcome these problems.

Ethanol is commonly used in the beverage industry. The concentration of alcohol in an alcoholic beverage may be specified in percent alcohol by volume (ABV) or in proof. The 'proof' measurement roughly corresponds in a 2:1 ratio to percent alcohol by volume (70 proof $\approx$ 35 % ABV). The fermented mixture which contains about 18 % alcohol is used for wine and beer. Distilled alcoholic beverages which contain at least 35 % alcohol by volume are referred to as spirits. These include gin, vodka, rum, whiskey and brandy. Fortified wines are produced by adding distilled spirits to achieve higher ABV.

Alcoholic beverages are added to dishes for their inherent flavours as well as their ability to dissolve flavour compounds that water cannot. They are used in many social and even religious events. Politicians, entertainers, athletes and other public figures are seen using alcoholic beverages. However, drinking alcohol in excess has become one of society's most serious problems.



IMPACT OF THE ALCOHOL INDUSTRY

Alcohol is one of the most frequently abused drugs. Business and government spend more money than is generated from sales of alcoholic beverages to address the abuse of alcohol consumption in society.

The effects of alcohol can contribute to work related problems such as excessive absence and poor performance on the job. Alcohol is associated with most crime. It is linked to murders, rapes, assaults and domestic violence. Many fatal accidents such as fire deaths, traffic accidents and drowning are associated with alcohol.

Alcohol is a depressant drug that affects the central nervous system. Temporary effects of alcohol are relaxation, loss of inhibition, slower reflexes and impaired coordination. Permanent effects are cirrhosis of the liver, heart diseases, cancer or gastrointestinal problems and addiction. About 0.5 % alcohol in the blood is toxic and when combined with medication or other drugs can result in death. Alcohol kills brain cells and may cause memory loss. Alcohol consumption during pregnancy may result in birth defects such as facial abnormalities, heart defects, abnormal limb development and brain damage which results in less than average intelligence.



The brain images below show how alcohol may harm teen mental function. Compared with a young non-drinker, a 15-year-old with an alcohol problem showed poor brain activity during a memory task. This finding is noted by the lack of pink and red colouring.



Considering the hazards presented by the consumption of alcohol, it is interesting to note how people do not reject alcoholic beverages. Instead, its popularity remains embedded in culture and society.



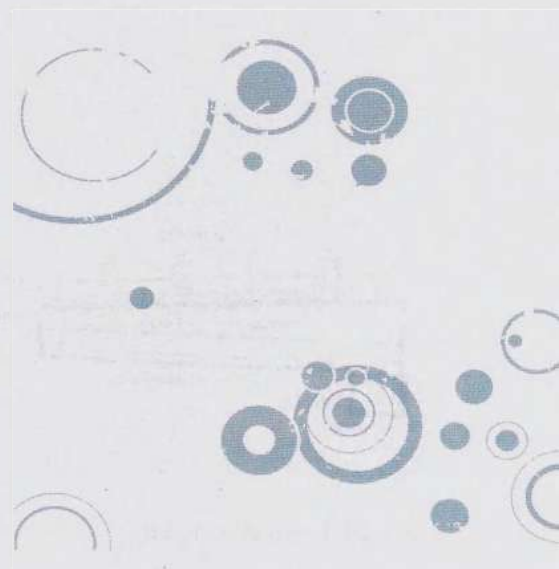
Traffic accident





Questions

1. Alcohol for human consumption is made via fermentation. This can be done industrially or at home. Fruits such as grapes and cherries can be used in the process.
 - (a) What chemical features do the starting materials like fruits possess?
 - (b) Different starting materials produce home-made alcoholic beverages with different characteristics. Name two different characteristics.
 - (c) Is alcohol a drug? Justify your answer.
2. The consumption of alcohol has serious consequences both socially and economically. Outline four social and economical consequences that originate from the consumption of alcohol.
3. State the importance of the following in the fermentation process:
 - (a) Yeast
 - (b) Temperature control
 - (c) pH control
4. Alcohol consumption has been blamed for many road accidents. Discuss this statement outlining the effects of alcohol on the body.



The chlor-alkali industry is the industry that produces chlorine and alkali, mainly sodium hydroxide, by electrolysis of a salt solution. The main processes used are the mercury, diaphragm and membrane cell electrolysis. The diaphragm and the mercury cell were both introduced in the late 1800s. The membrane cell process was developed much more recently (1970). Each of these processes represents a different method of keeping the chlorine produced at the anode separate from the sodium hydroxide and hydrogen produced at the cathode. If they are not separated, the hydrogen and chlorine would ignite spontaneously and the sodium hydroxide and chlorine would react to form sodium hypochlorite.

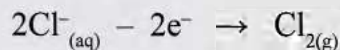


THE MERCURY CELL

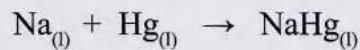
The mercury cell consists of two compartments, one on top of the other. Each compartment is lined with a flowing mercury cathode. Saturated brine flows through the top compartment. Graphite or titanium anodes are suspended in the brine.

An electric current flowing through the cell decomposes the brine. Chlorine gas is liberated at the anode and sodium metal is produced at the cathode. The sodium immediately forms an amalgam with the mercury.

At the anode



At the cathode



The amalgam flows to the lower compartment where it reacts with water to form sodium hydroxide, hydrogen gas and mercury. The mercury is then pumped to the top compartment where it is reused. However the cell inherently gives rise to the release of mercury into the environment.

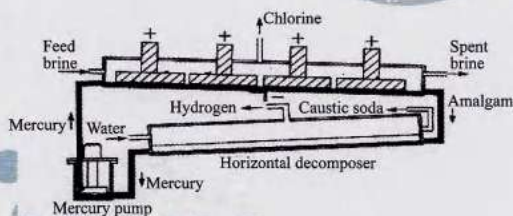
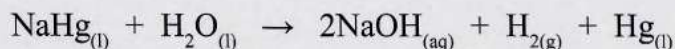


Fig. 38.1 A mercury cell





THE DIAPHRAGM CELL

In the diaphragm cell chlorine, sodium hydroxide and hydrogen are produced simultaneously. The anode and cathode compartments of the cell are separated by a porous diaphragm. Saturated brine enters the anode compartment and percolates through the diaphragm into the cathode chamber. The percolation rate is controlled by maintaining a higher liquid level in the anode compartment so that there is a small positive pressure towards the cathode. Chlorine gas is liberated at the anode and hydrogen gas at the cathode, leaving sodium hydroxide in solution.

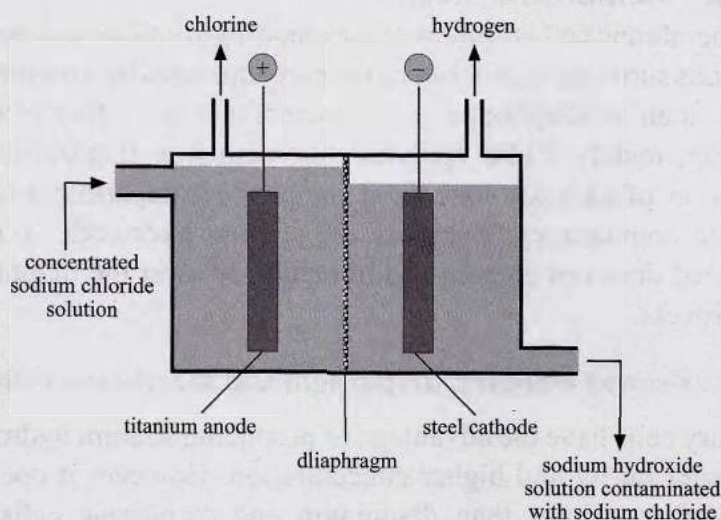
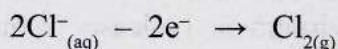
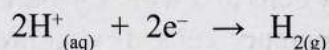


Fig. 38.2 A diagram of a diaphragm cell

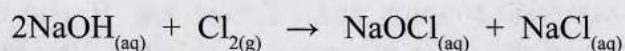
At the anode



At the cathode



The diaphragm is used to separate the chlorine liberated at the anode from the hydrogen and sodium hydroxide produced at the cathode chamber. Without the diaphragm to isolate them, the hydrogen and chlorine would ignite spontaneously and the sodium hydroxide and chlorine would react to form sodium hypochlorite.



In practice, the solution in the cathode chamber is a mixture of sodium hydroxide and sodium chloride. On partial evaporation, the sodium chloride is crystallized out leaving concentrated



sodium hydroxide. The sodium chloride is recycled through the cell.

Graphite anodes shorten the lifetime of the diaphragm by plugging the diaphragm with particles of graphite. When metal anodes are used the lifetime of the diaphragm is lengthened. Diaphragms are usually made of asbestos. Asbestos is chosen because of its good chemical stability and it is a relatively inexpensive and abundant material. The diaphragm cell therefore inherently gives rise to the releases of asbestos in the environmental.



MEMBRANE CELL

The membrane cell is similar to the diaphragm cell except that the solutions surrounding each electrode are separated by a membrane rather than a diaphragm. The membrane is a fluorocarbon polymer, mainly PTFE (polytetrafluoroethene). It prevents the migration of chloride ions from the anode compartment to the cathode compartment therefore the sodium hydroxide solution produced does not contain sodium chloride as in the diaphragm cell process.

Comparison of mercury, diaphragm and membrane cells

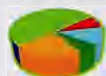
Mercury cells have the advantage of producing sodium hydroxide of greater purity and higher concentration. However it operates at a higher voltage than diaphragm and membrane cells and therefore uses more energy. The process also requires a pure brine solution of a high purity, which often requires costly additional purification steps prior to electrolysis. Furthermore the mercury cell gives rise to environmental releases of mercury.

Diaphragm cells have the advantage of operating at a lower voltage than mercury cells and with less pure brine than required by membrane and mercury cells. It also produces chlorine gas with nearly no oxygen. The capital cost is relatively less expensive than the mercury cells. Disadvantages of the diaphragm cell are that the sodium hydroxide produced may need to be evaporated to increase concentration and it gives rise to environmental releases of asbestos.

Membrane cells have the advantage of producing a very pure sodium hydroxide solution and chlorine gas. It also uses less electricity than the other processes. In addition, the membrane process does not use highly toxic materials such as mercury and asbestos. Disadvantages of the membrane process are that the sodium hydroxide produced may need to be evaporated to



increase concentration and the brine entering a membrane cell must be of a very high purity.



USES OF CHLORINE

The largest use of chlorine is in the production of organic compounds such as poly vinyl chloride (PVC) and chlorofluorocarbons (CFCs). PVC is used extensively to make items such as plastic pipes, tubing, bags and toys. The demand for PVC is high in the construction, packaging, and other industries since it does not rust or decompose.

CFCs were once widely used as refrigerants and propellants in aerosols. This resulted in large emissions in the atmosphere which contributed to the depletion of the ozone layer. Refrigerants and aerosols are being replaced by hydrofluorocarbons (HFCs) which do not deplete the ozone layer.

CFCs are also used as anaesthetics in medicine. Halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) is a common anaesthetic used in surgery. It allows operations to be safe for patient. It is not poisonous and can allow surgery to last for hours. After surgery, the anaesthetic itself wears off fairly quickly and has relatively few side effects.

Chlorine is also used as a disinfectant in water treatment. It kills bacteria and other microbes from drinking water supplies and swimming pools. It is used to make household bleach and other compounds to bleach wood pulp in paper production.

Chlorine is used to make solvents for dry cleaning, metal work and the electronics industry. It is also used in the manufacture of products such as antiseptic, dyes, insecticides and paints.



Chlorine is used to make PVC which is used to make toy items.



Water in swimming pools is treated with chlorine.



IMPACT OF THE CHLOR-ALKALI INDUSTRY

The pollutant of most concern from the chlor-alkali industry is mercury, which is specific to the mercury cell. Between 1930 and 1960, several tonnes of mercury waste were dumped in Minamata Bay in Japan. Thousands of people living around the bay developed methyl mercury poisoning through the consumption of contaminated fish. Since then, there was a significant move away from mercury-cell to diaphragm and membrane cells. Japan was the first country to install the membrane cells on a massive scale in the mid-1980s. In other countries, the replacement of existing



The crippled hand of a Minamata disease victim.



mercury and diaphragm cell with membrane cells is taking place at a slower rate because of the high capital costs of replacement and the fact that most existing chlorine plants were installed with a plant life of 40-60 years.

The main problem with the diaphragm cell is asbestos. Dry asbestos fibres can cause serious health problems if not properly used and handled in the diaphragm process. Asbestos fibres are thin, sharp crystals, which are considered to be carcinogenic. They can enter the human body by either inhalation or ingestion.

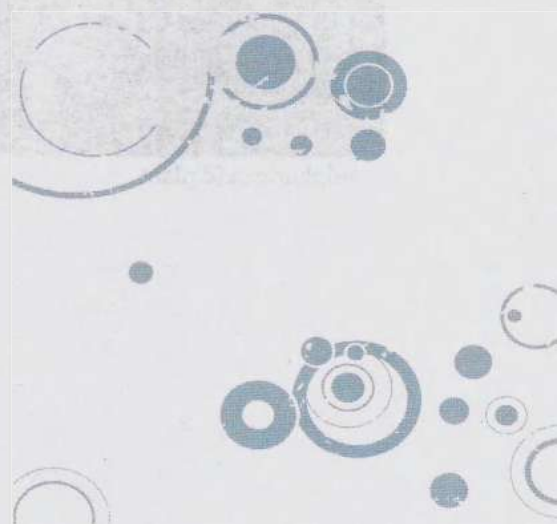
Other concerns of the chlor-alkali industry are associated with the chemical processes that use chlorine. Chlorine bleaching of wood pulp releases dioxins in the environment. The production of chlorofluorocarbons (CFCs) contributes to depletion of the ozone layer. PVC is not biodegradable and generates dioxins and hydrogen chloride gases when it is incinerated.





Questions

1. Give an account of the electrolysis of brine using a diaphragm cell. Include the equations for the reactions at the electrodes and the overall process.
2. The flowing mercury cathode cell is used in the production of chlorine from concentrated aqueous sodium chloride.
 - (a) Write equations for the reactions at the electrodes.
 - (b) Write an overall equation for the process.
 - (c) Give two advantages and one disadvantage using the mercury cathode cell.
 - (d) What are the by-products of the process?
 - (e) State the use of one of the by-products named in (d) above.
3. Electrolysis using the mercury cathode cell produces chlorine as the major product.
 - (a) State the type of anode used.
 - (b) Give an addition function of the mercury.
 - (c) Compare the use of a mercury cell with that of a diaphragm cell in terms of energy consumption, economic cost and environmental concerns.
 - (d) Discuss the impact of the chlor-alkali industry on the environment.





THE CONTACT PROCESS

Sulphuric acid is produced commercially using the Contact process. The raw materials needed are a source of sulphur dioxide, air, water and a catalyst. The main stages in the process are:

- production of sulphur dioxide
- oxidation of sulphur dioxide to sulphur trioxide
- hydration the sulphur trioxide to sulphuric acid.

Production of sulphur dioxide

This can be produced by:

- burning sulphur in an excess of air

$$\text{S}_{(s)} + \text{O}_{2(g)} \rightarrow \text{SO}_{2(g)}$$
- heating sulphide ores like pyrite in an excess of air

$$4\text{FeS}_{2(s)} + 11\text{O}_{2(g)} \rightarrow 2\text{Fe}_2\text{O}_{3(s)} + 8\text{SO}_{2(g)}$$
- decomposing calcium sulphate in the presence of coke

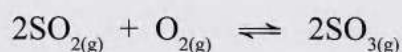
$$2\text{CaSO}_{4(s)} + \text{C}_{(s)} \rightarrow 2\text{CaO}_{(s)} + \text{CO}_{2(g)} + 2\text{SO}_{2(g)}$$



A sulphuric acid plant

Oxidation of sulphur dioxide to sulphur trioxide

Sulphur dioxide is mixed with excess air and passed through an electrostatic precipitator which removes dust and impurities. The purified sulphur dioxide combines with oxygen in the presence of a catalyst, vanadium (V) oxide, to form sulphur trioxide, the anhydride of sulphuric acid.



$$\Delta H = -196 \text{ kJ mol}^{-1}$$

This is a reversible reaction which means the reactants and products reach a state of dynamic equilibrium. Since the reaction is exothermic and results in a decrease in volume i.e. three moles of reactants form two moles of products, according to Le Chatelier's Principle, low temperature and high pressure would shift the position of equilibrium to the right and increase the yield of sulphur trioxide. Thus the forward reaction will be favoured by a low temperature and a high pressure. However,



at low temperatures, the reaction rate would be too slow to be economical and at high pressures the sulphur dioxide liquefies.

A compromised temperature of about 450°C is used with a catalyst which produces a fairly high yield of sulphur trioxide at an acceptable reaction rate. The catalyst has no effect on the position of the equilibrium. It only increases the rate of the reaction. The catalyst is layered and is in the form of pellets to increase the surface area available for the reaction. Dust and impurities are removed from the gaseous mixture to prevent 'poisoning' of the catalyst. These reduce the surface area of the catalyst and decrease its efficiency. The Contact process gets its name from the fact that the reaction takes place by contact of the gaseous mixture with the surface of the solid catalyst.

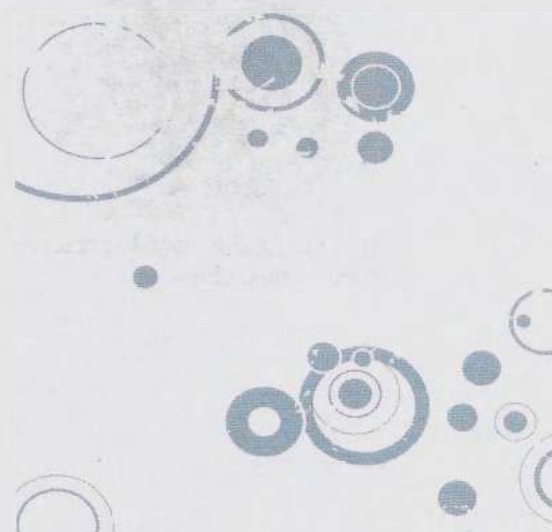
It must be noted that since the forward reaction is exothermic, the temperature of the surrounding system increases from 450°C to about 600°C as the reaction proceeds. At this temperature, the yield is reduced to approximately 70%. Therefore, the gases are cooled down to roughly 450°C between successive layers of catalyst to give a yield of approximately 98%. The cooling system is usually a closed water circuit in which energy is recovered as steam. Heat exchangers utilize the heat lost in the cooling process to heat the incoming gases and thus reduce the use of external heating.

Although high pressure gives a higher yield of sulphur trioxide in the equilibrium mixture, the reaction is done close to atmospheric pressure which gives an approximate yield of 98%. The cost and maintenance of equipment for production at higher pressures is not worth any further increase in yield of sulphur trioxide.

According to Le Chatelier's Principle, the forward reaction is favoured by increasing the concentration of oxygen in the mixture. This is a very cheap way of increasing the conversion of sulphur dioxide into sulphur trioxide since the oxygen comes from the air. A 1:1 mixture turns out to give the best possible overall yield of sulphur trioxide.

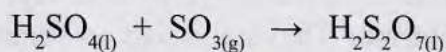
Hydrating the sulphur trioxide to sulphuric acid

In the industry, a gas is usually dissolved in water using a counter flow system in which water is sprayed downwards over the gas which is flowing upwards. This method cannot be used in the case of sulphur trioxide because the reaction is highly exothermic and creates uncontrollable clouds of sulphuric acid which are difficult to condense. Concentrated sulphuric acid destroys skin and flesh,

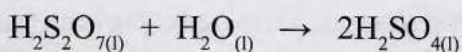


and can cause blindness if it gets into the eyes.

Instead, the sulphur trioxide is first dissolved in concentrated sulphuric acid to form oleum.



This can then be diluted with water to produce concentrated sulphuric acid.



USES OF COMPOUNDS OF SULPHUR

Most sulphur is used to produce sulphur dioxide to make sulphuric acid. Sulphur is also used in the vulcanization of natural rubber to improve its elasticity and tensile strength. This process makes the rubber less sticky and less soluble in organic solvents. Other uses of sulphur are as a fungicide and as a fumigant.



Sulphur dioxide used to preserve dried banana chips.

Sulphur dioxide is a reducing agent and is used for bleaching wool, straw and paper. The bleaching effect is usually temporary as oxygen in the atmosphere can re-oxidize the reduced material. This explains why white newspaper turns yellow after some time.

Sulphur dioxide is useful as an antioxidant in food preservation. It is sometimes used as a preservative in alcoholic drinks and dried fruits. It prevents growth of moulds and its acidity also kills bacteria.

The main use of sulphur dioxide is in the manufacture of sulphuric acid. Sulphuric acid is commonly used in the manufacture of fertilizers, detergents, car batteries, high strength fibres, paints and pigments. It is also used in petroleum refining and metallurgy.



IMPACT OF THE SULPHURIC ACID INDUSTRY

Since some sources of sulphur dioxide are the by-product of other processes such as the extraction of metals from sulphide ores and the decomposition of calcium sulphate in the manufacture of cement, sulphuric acid production reduces sulphur dioxide emissions to the atmosphere. However emission of sulphur dioxide from the Contact process is minimized by recycling unreacted sulphur dioxide and scrubbing tail gas with a basic solution such as ammonium or sodium hydroxide. Sulphur dioxide in the atmosphere is converted to acid rain (see page 474).

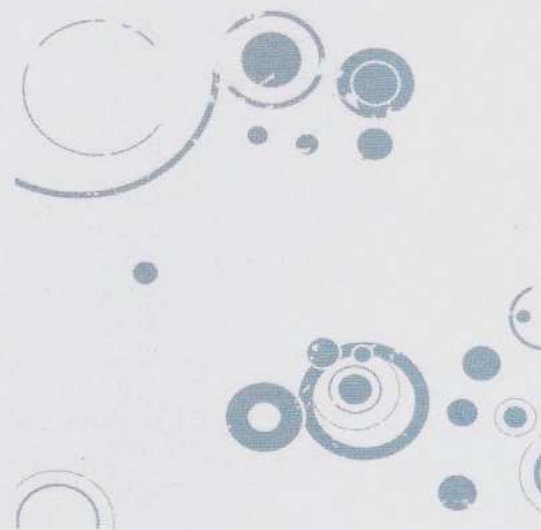


Large amounts of sulphuric acid are used as catalysts in the chemical industry and needs to be replaced with fresh concentrated acid when diluted or contaminated. The spent sulphuric acid from the chemical industry is regenerated and recycled. Thermal decomposition of spent sulphuric acid gives sulphur dioxide which is regenerated into clean sulphuric acid which can be reused in any process.

Spent catalyst from the Contact process can be either disposed in a suitably licensed landfill site or its vanadium content can be recovered and recycled. Regeneration and recycling are different ways to prevent spent acid and catalyst from becoming a waste and a problem for the environment.

Sulphuric acid production is a net producer of energy. Heat evolved in the process is used to turn water into steam which is used to generate electricity. No carbon dioxide is formed as fossil fuel is not used.

During production, handling and storage of sulphuric acid there is always a risk of accidental leaks which may have an impact on the environment. Precautions have to be taken to reduce these possibilities.

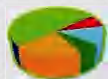




Questions

1. In the Contact process, sulphur dioxide is produced in an intermediate stage. Concerns have been raised as to the effects of sulphur dioxide on the environment.
 - (a) Give a detailed account of the Contact process including the sources of all the raw materials and the chemistry of the process.
 - (b) State the major effect of the presence of sulphur dioxide in the atmosphere.
2. In industries sulphur dioxide is reacted with other reagents in an attempt to remove it from flue gases. These reagents are called “scrubbers”. Write an equation to show how calcium carbonate acts as a scrubber, explaining the process fully.
3.
 - (a) Describe the Contact process for the manufacture of sulphuric acid. Your answer should include the raw materials used, the reaction conditions and balanced relevant equations.
 - (b) Le Chatelier’s principle suggest that an increase in pressure and a decrease in temperature will increase the yield of sulphur trioxide in the Contact process. Justify the choice of conditions for the Contact process in the industry.
 - (c) Explain the functions of vanadium pentoxide, successive beds of catalysts and oleum in the Contact process.
4. Although sulphur dioxide is a major atmospheric pollutant it is used in the food and drink industry.
 - (a) State one reason why it is used in some foods and drinks.
 - (b) Name two sources of sulphur dioxide as an atmospheric pollutant.
 - (c) What are the consequences of sulphur dioxide in the atmosphere?
 - (d) How can sulphur dioxide emissions be controlled?





THE WATER CYCLE

The water cycle, also known as the hydrologic cycle, is a natural process by which water is continually exchanged between the surface of the Earth and the atmosphere. Water naturally exists as a solid, liquid or gas on the Earth and is cycled through nature in these forms. It uses energy from the Sun to change its state.

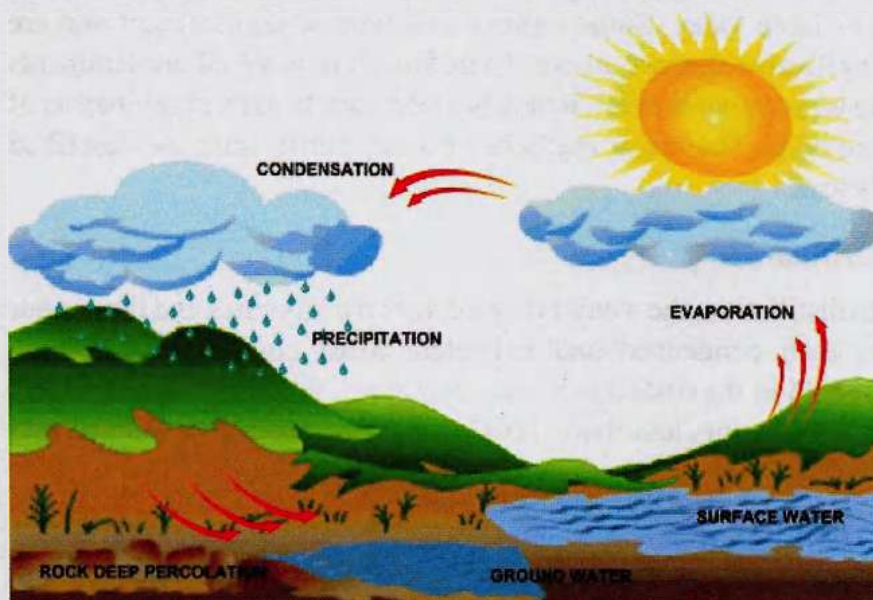


Fig. 40.1 The water cycle

Water on the surface of the Earth such as lakes, rivers and oceans enters the atmosphere by evaporation. It then condenses to form clouds and falls back down to Earth by precipitation. Rain is one form of precipitation. If the clouds are cold enough precipitation may occur as snow or hail. Precipitation that falls on the surface of the Earth can once again evaporate so that the cycle starts all over again.

Importance of the water cycle

The water cycle is a natural self-purifying system that is vital to all living things. Without the continuous return of fresh water to the Earth, organisms could not exist. The water cycle provides fresh water for drinking, agriculture, industry and domestic use.



It also replaces water lost by lakes, rivers and oceans which are habitats for many organisms. Furthermore, the water cycle affects the climate on Earth. It regulates the temperature by absorbing heat from the equator and circulating it around the Earth.



WATER PURIFICATION



Clean drinking water

Water from natural sources in the environment is called raw water. It is treated or purified to remove contaminants to produce water suitable for domestic consumption. Many contaminants such as micro-organisms and toxic metals are a health hazard and are removed during water purification. Other contaminants may be removed to improve the taste, smell and appearance of the water. There are many different methods of water purification available today. Some remove one type of contaminant and are ineffective against others. Therefore to remove all contaminants to an acceptable level, it may be necessary to use a combination of methods. The major methods of water purification are described below.

Distillation

In distillation, the water is heated until it evaporates and the vapour is then condensed and collected. Most contaminants remain behind in the distilling vessel. However, volatile impurities with boiling points less than 100°C can evaporate and be carried into the distillate.

Distillation removes a wide range of contaminants from water. These include bacteria, sodium chloride, heavy metals and organic compounds. The equipment is relatively inexpensive but it requires careful maintenance to ensure purity of water. In addition, the process is slow and it requires large amounts of energy.

Ion exchange

In the ion-exchange process, water percolates through a column of spherical resin beads. The ions in the water are exchanged for the ions fixed to the beads. Common ion-exchange methods are softening, deionization and electrodeionization.

Softening

Softening ion-exchange resins are generally used to remove calcium and magnesium ions from hard water. The ion-exchange resins contain adsorbed sodium ions. As hard water percolates through the column, the calcium and magnesium ions are



exchanged for the adsorbed sodium ions on the resin beads. The soluble sodium ions remain in the softened water.



The resins can be regenerated by washing with concentrated aqueous sodium chloride.



Deionization

Deionization removes dissolved minerals from water. The ion-exchange resins contain adsorbed acid or alkali. The acidic resin exchanges hydrogen ions for cationic contaminants while the alkaline resin exchanges the hydroxyl ions for anionic contaminants in water. The resins can be regenerated by washing with an acid or alkali.

Electrodeionization

In electrodeionization, water is effectively deionized while the ion exchange resins are continuously regenerated by an electric current in the system. The electric current splits water molecules into hydrogen ions and hydroxyl ions which continuously regenerate the resins. The contaminants migrate through the resin and are removed from the system.

This technology eliminates chemical regeneration of resins with acid and alkaline. Thus the system can operate continuously without shutting down to regenerate the resins. The resins do not get exhausted and lose efficiency which allows it to produce water of consistent purity.

Softening and deionization remove ions effectively but they do not remove most organic compounds or micro-organisms. Bacteria can attach to the resins which provide a suitable medium for its rapid growth. However, in electrodeionization the electrical conditions within the system inhibit the growth of micro-organisms.

Filtration

Filters are used to remove suspended material from water. There are several different filtration techniques utilized in water purification. These include screen filtration, sand filtration, carbon adsorption and membrane filtration. The filtration method implemented depends upon the types of contaminant that needs to be removed and their particle size.



Screen filters

Screen filters are used mainly to remove large debris such as sticks, leaves and trash from the water. The screen is made of a metal, plastic or synthetic fiber mesh enclosed in a frame. The design is of various shapes and sizes to allow for the separation of larger particles in the water.

Sand filters

Sand filters are layers of sand or other suitable granular material used to reduce suspended solids from water. As the water moves vertically through the sand, suspended solids are trapped in the sand. The efficiency of sand filters depends on the particle size of the sand, the ratio of surface area to depth of the filter and the flow rate of water through the filter. Sand filters can be used as a pre-filtration method for membrane systems.

Carbon filters

Carbon filters use pieces of charcoal to remove contaminants from water. They effectively reduce sediments, volatile organic compounds (VOCs) and chlorine from water. The charcoal is usually activated with a positive charge which causes organic contaminants in the water to adsorb onto its surface. It also catalyzes the conversion of chlorine to chlorides, and hydrogen sulphide to sulphates which reduces undesirable odours and tastes in water. In addition, removal of chlorine is important in that it prevents degradation of resins and membranes in other purification methods.

New carbon filters on the market can remove micro-organisms and fine sediment particles down to 0.5 micrometres. However, they do not remove most inorganic compounds from water. Therefore carbon filters are often used as a pre-treatment method for ion exchange and membrane filtration.

Membrane filtration

Membrane filtration utilizes a semi-permeable membrane and pressure to filter water. It includes micro filtration, ultra filtration and reverse osmosis. The membrane for each type of filtration is rated for a particular particle size. The standard size rating is in microns (micrometres). Contaminants are removed from water depending on the micron rating of the membrane. Membranes with pore size of 0.2 micron are widely used in micro filtration while ultra filtration uses membranes with pore sizes which range from 0.02 to 0.001 microns. Micro filters and ultra filters separate



A countertop carbon water filter



contaminants on the basis of size by passing the water through the extremely fine membrane. Table 40.1 below shows the membrane size required to remove some common micro-organisms.

Table 40.1

Common micro-organisms and the membrane size needed:

Organism	Examples	General Size	Membrane size rating
Protozoa	Giardia, Cryptosporidium	5 microns or larger	4.0 microns
Bacteria	Cholera, E. coli, Salmonella	0.2 – 0.5 microns	0.2 microns
Viruses	Hepatitis A, rotavirus	0.004 microns	0.004 microns

Reverse osmosis uses an external pressure to force water through a membrane that retains the solute on one side and allows the pure water to pass through to the other side. The process forces water molecules from a region of high solute concentration through a membrane to a region of low solute concentration. This is the opposite of natural osmosis where water molecules move from a region of low solute concentration to a region of high solute concentration through a semi-permeable membrane.

Reverse osmosis uses the finest available membrane for filtration. It requires a high enough pressure to pump the water in the opposite direction of natural osmosis. The membranes are designed to allow water to pass through but restrict solutes, bacteria and other microscopic particles. It is even capable of removing dissolved inorganic salts.

This technology efficiently removes all types of contaminants with the exception of dissolved gases. However, since the membranes are so restrictive, the process is limited by the relatively slow rate of purifying water. In addition, productivity is low as a large portion of the water that is fed into the system is run out with the waste contaminants.

Chemical treatment

Chemical treatment in water purification includes clarification and disinfection.

Clarification

Clarification works by using chemicals to coagulate and flocculate

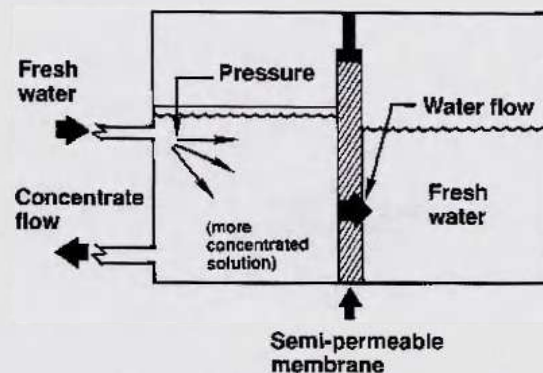


Fig. 40.2 Reverse Osmosis





small suspended particles together in the water. Common coagulants used are aluminum sulphate (alum), iron (III) sulphate and iron (III) chloride. Coagulants cause small suspended particles to flocculate or clump together into larger particles called flocs. The flocs either sink to the bottom or float to the top of the water so that they can be removed. The clarified water may still contain some suspended particles and therefore needs further treatment.

Disinfection

Disinfection is usually the last step in water treatment plants. Water is disinfected with chlorine gas, chloramine, sodium hypochlorite, chlorine dioxide or ozone to kill any pathogens which pass through the filters.

Although chlorine kills many pathogens, cyst forming protozoa like *Cryptosporidium* and *Giardia* are resistant to it. In addition, there is growing concerns over its reaction with organic compounds in the water to form chlorinated organic products such as trihalomethanes (THMs) and haloacetic acids (HAAs) which are carcinogenic.

Using an activated carbon filter after chlorination can remove excess chlorine and limited amounts of chlorinated compounds formed in water. However, chlorine dioxide (ClO_2) is preferred to treat drinking water as it does not produce THMs. Other halogens such as fluorine and iodine are not safe for long-term usage in water treatment. Iodine in particular, can affect persons with thyroid disease.

Unlike chlorine, ozone is effective at destroying cyst forming protozoa. It also produces relatively fewer harmful by-products compared to chlorine. Moreover ozone leaves no residual disinfectant in the water.

UV radiation

UV light is very effective at killing pathogens and oxidizing organic compounds in water. Radiation with a wavelength of 254 nm has the greatest effect on bacteria however viruses are more resistant, and cysts and worms are unaffected. Radiation with wavelengths 185 nm is most effective for the oxidation of organic compounds. Like ozone treatment, UV radiation leaves no residual disinfectant in the water.

Desalination

Desalination refers to any technology that removes salt from



water. The two main methods used are distillation and reverse osmosis. With either technology, desalination produces fresh water and concentrated brine.

There are some environmental concerns with desalination plants. Firstly, the brine effluent is about twice as salty as the ambient seawater and when it is discharged into the sea it may create localized areas that are too salty for sea life. Secondly, water taken in from the ocean usually results in loss of marine life when organisms collide with screens at the intake position. Also organisms which pass through the screens are killed during the water treatment process. Desalination of ocean water is common in places like the Middle East and the Caribbean.

Importance of dissolved oxygen to aquatic life

The concentration of dissolved oxygen in water is one of the most important features of water quality. Oxygen can dissolve in water directly from the atmosphere and during photosynthesis of aquatic plants. Fish and other aquatic life need dissolved oxygen in the water to survive. It is used by aquatic organisms for respiration and by the aerobic bacteria for decomposition.

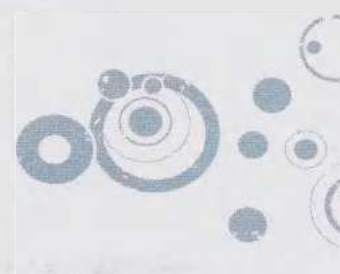
Dissolved oxygen in water is measured in parts per million (ppm) and range from 0-18 ppm. Most natural waters require 5-6 ppm of dissolved oxygen to support a variety of aquatic life. If dissolved oxygen falls to 3-5 ppm aquatic life becomes stressed. Dissolved oxygen below 2 ppm can result in death of aquatic organisms.

The level of dissolved oxygen is decreased in the following processes:

- **Respiration** – increase in aerobic respiration decreases the oxygen concentration dissolved in water. Microbial pollution from improperly treated sewage can increase microbial respiration in water and thus decrease dissolved oxygen levels. The amount of oxygen used by these organisms to decompose the waste is known as the biological oxygen demand or BOD.
- **Temperature** – as temperature increases, the amount of oxygen dissolved in water decreases. This means that as global warming increases the temperature of natural bodies of water, less oxygen is dissolved in the warm water.
- **Eutrophication** – excess nutrients in water can stimulate algal growth on the surface of water. When these plants die, bacteria use dissolved oxygen in the water for decomposition.



A desalination plant



These processes can lead to dissolved oxygen being reduced to dangerously low levels. As a result, fish and other aquatic animals that rely on oxygen for respiration may die.



SOURCES OF WATER POLLUTION

Water pollution occurs when bodies of water are adversely affected due to human activities. Natural phenomena such as volcanoes and earthquakes can cause major changes in water quality however these are not considered to be pollution. The major sources of water pollution can be classified as municipal, agricultural and industrial.

Municipal

This generally arises from sewage from homes and commercial establishments. Sewage is the term used for wastewater which flushes down the toilets and sinks. It is carried along sewage pipes to sewage treatment plants where it is treated and disposed in the environment. Untreated sewage or poorly treated sewage can pollute the environment.

In developing countries, an estimated 90% of wastewater is discharged directly into rivers and streams without treatment. Untreated sewage water in such areas can spread diseases caused by microbes such as viruses, bacteria, and intestinal parasites. Diarrhea, dysentery, cholera and tuberculosis are some diseases that can be transmitted in water.

Organic waste in sewage is biodegradable and utilizes the dissolved oxygen in water for decomposition. Furthermore, phosphate from laundering water enhances algal bloom which also causes eutrophication.

Dumping of garbage in water is another serious problem. Items such as plastic packaging materials and synthetic fibers can entangle, injure and even kill aquatic animals. In addition, biodegradable garbage depletes water of dissolved oxygen when decomposition occurs.

Agricultural

Indiscriminate use of fertilizers, herbicides and pesticides in agriculture indirectly contribute to water pollution. Rainfall or irrigation washes nitrate and phosphate fertilizers from the soil into waterways. These nutrients enhance algal bloom which causes eutrophication.



A polluted river in Jakarta, Indonesia. It is a main source of water for Jakarta regional and municipal water supplier.



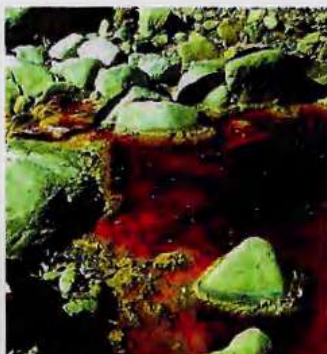
Herbicides and pesticides also wash into groundwater and surface water. These contaminants can remain in the water for many years and spread over a large area before degradation occurs. Since herbicides and pesticides are designed to kill plants and animals, they are lethal to aquatic organisms. Drinking water contaminated with these chemicals has a variety of effects on man which may include diarrhea, vomiting, skin and eye irritation and risk of cancer.

Industrial

Waste from industries often contains toxic chemicals that are discharged directly or indirectly into the water system. Industrial sources of pollution include:

- **Nuclear waste** — nuclear power stations produce radioactive waste which pollutes water. Radioactive traces from plants in Europe have been found as far as Greenland.
- **Oil spills** — these may occur during extraction, transportation and refining of the crude oil. In 1989 the Exxon Valdez oil spill off the coast of Alaska caused major water pollution that was catastrophic to local marine wildlife such as fish, sea otters, seals, and sea birds.
- **Lead** — it enters the environment as waste from smelting, car batteries and plumbing industries. Lead leaches into water from underground lead pipes and lead solder used in copper pipes. Brass plumbing materials also contain lead which contaminates water. Lead is a cumulative poison and is not excreted from the body. It causes brain damage, especially in children.
- **Mercury** — this pollutant enters the environment as waste from the chlor-alkali industry, burning of coal and mining. Fluorescent light bulbs, thermometers and other scientific apparatus that contains mercury eventually contaminate water supplies when thrown away in garbage. Mercury builds up in the tissues of fish and accumulates as it moves up the food chain. This cumulative poison eventually affects the nervous system of man. At dangerously high levels it can cause death.
- **Mining** — this is the extraction of naturally occurring minerals from the earth. The process allows heavy metals and other toxic compounds to be exposed





Drainage from the Iron Mountain Mine

on the surface of the earth. Rainwater leaches these compounds out of the surface of the earth which run off into natural waterways. Gold mining uses cyanide to chemically extract the gold from the ore. Some of this cyanide eventually finds its way into water sources. Water pollution usually continues long after the mining operations have ceased. This can be seen at Iron Mountain mine in California which has been closed since 1963 but continues to leach sulphuric acid and heavy metals such as zinc and cadmium into the Sacramento River. No life exists in this water which has an orange colour and a pH value well below zero (i.e. the concentration of H^+ ions is more than 1 mol dm^{-3}).

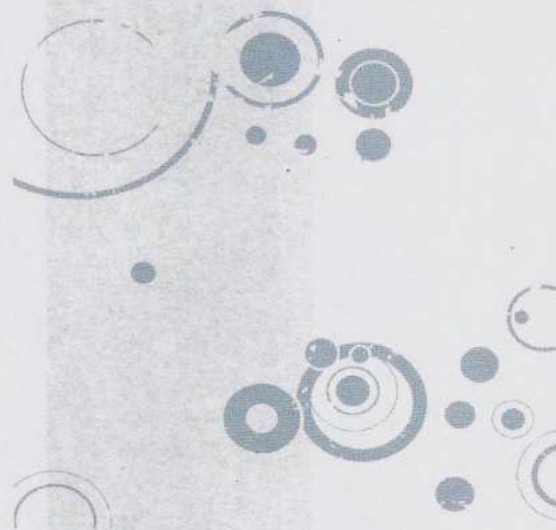




Questions

- With the aid of a diagram describe the water cycle.
 - Explain the importance of the water cycle in nature.
- Describe the following methods of water purification:
 - Reverse osmosis
 - UV radiation
 - Desalination
- List two methods of water purification. Discuss the advantages and disadvantages of each of the method named.
- The concentration of dissolved oxygen in water is a significant feature of water quality. Discuss the importance of dissolved oxygen to aquatic life.
- Suggest how the following substances can enter waterways.
 - Nitrates
 - Mercury
 - Pesticides

Discuss how the presence of these substances in water affect living organism.





LAYERS OF THE ATMOSPHERE

The layer of gases that surrounds the Earth is called its atmosphere. These gases keep our planet warm and protect us from the harmful radiation of the Sun. Earth could not sustain life without its atmosphere.

The atmosphere is divided into four distinct layers based on temperature. With increasing distance from the surface of the Earth, these are the troposphere, the stratosphere, the mesosphere and the thermosphere. The atmosphere becomes thinner with altitude and eventually fades off into outer space.

The troposphere

This layer extends to about 15 km above the surface of the Earth. The air is mainly composed of nitrogen (78%), oxygen (21%) and other gases (1%). It is the air we breathe. Not included in the above air is water vapour which is highly variable (1% - 4%). Nearly all atmospheric water vapour is found in the troposphere.

The troposphere is associated with weather conditions. The changes in temperature, wind, pressure, and moisture in this region are created as a result of the rotation of the Earth about its axis and convection currents generated as the surface of the Earth is heated by solar radiation. The troposphere helps keep the Earth warm and maintain its climate.

Generally, the temperature decreases with altitude in the troposphere. This is due to the decrease in heat transfer by convection as the distance from the surface of the Earth increases. In addition, as the pressure decreases with altitude, rising gases expand and cool. This makes the top of the troposphere an extremely cold and windy place.

The stratosphere

The stratosphere is a stable layer of atmosphere which extends from about 15 km to 60 km above the surface of the Earth. It contains a relatively high concentration of ozone which is constantly being formed and broken down through interactions with ultraviolet radiation. These overall reactions are exothermic and warm up

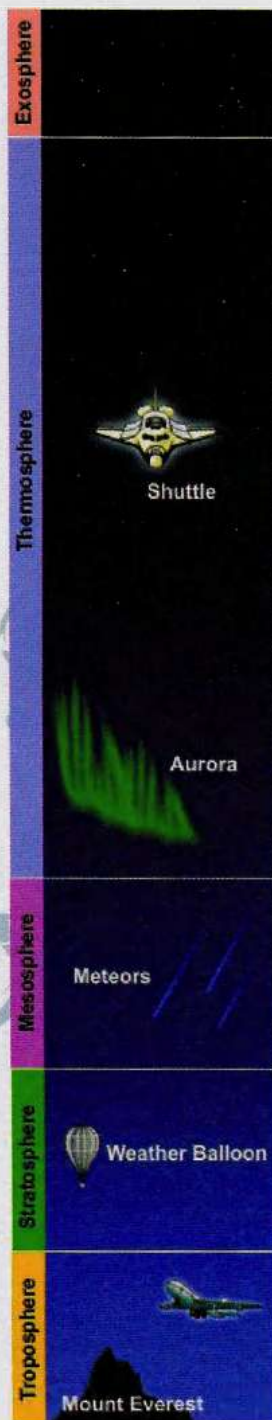


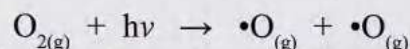
Fig. 41.1

Layers of the atmosphere

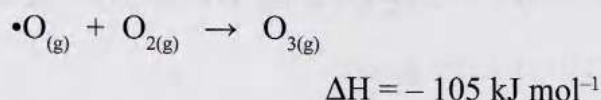


the atmosphere in this layer. Therefore the temperature increases with altitude in the stratosphere.

Ozone is formed from a pair of photochemical reactions. First molecular oxygen absorbs ultraviolet radiation (wavelengths < 242 nm) to form two oxygen free radicals.

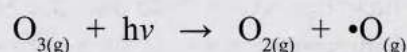


Then the oxygen free radicals react with molecular oxygen, in an exothermic reaction, to form ozone. This reaction usually takes place in the presence of an inert body such as nitrogen.

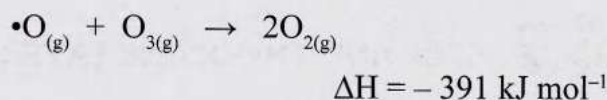


The inert body carries away the excess energy which would otherwise cause the ozone to breakdown back to molecular oxygen and oxygen atoms.

Ozone is broken down by another pair of photochemical reactions. First ozone absorbs ultraviolet radiation (wavelengths 290-330 nm) and undergoes photodissociation to form molecular oxygen and oxygen atoms.



Then the oxygen atoms react with ozone, in an exothermic reaction, to form molecular oxygen.



In the stratosphere, these photochemical reactions occur because the intensity of ultraviolet radiation is high enough to dissociate oxygen and ozone molecules significantly. However, in the troposphere the ultraviolet radiation is insufficient to dissociate molecular oxygen as most of the high intensity ultraviolet radiation would have already been absorbed in the stratosphere. Above the stratosphere, the concentration of molecular oxygen is too low to react with oxygen free radicals to form ozone thus the oxygen free radicals generally recombine to form molecular oxygen. Therefore an ozone layer is maintained about 25 km to 40 km above the surface of the Earth.

The photochemical reactions involved in the formation and destruction of ozone absorb a significant amount of high intensity



solar ultraviolet radiation. Thus the ozone layer prevents harmful ultraviolet radiation from reaching the surface of the Earth. This is very important to all living things on Earth, since unfiltered radiation from the Sun can destroy living tissue and increase the incidence of skin cancer and cataracts.

The mesosphere

The mesosphere extends from about 60 km to 80 km above the surface of the Earth. In this layer, the temperature once again begins to decrease with altitude. This is the coldest part of the atmosphere with temperatures reaching as low as -143°C . Here, meteors coming too close to earth slows down and burn up.

The thermosphere

The thermosphere extends from about 80 km to 500 km above the surface of Earth. It is the layer of the atmosphere which is first exposed to the solar radiation. The air is so thin that a small increase in energy causes a large increase in temperature. Here, the temperature reaches as high as 2000°C .

The solar radiation in the thermosphere causes air particles to become ionized. These charged particles form a layer called the ionosphere. Beautiful coloured lights called auroras are formed in the ionosphere near the North Pole and the South Pole. These are created in the ionosphere when solar radiation interacts with the magnetic field of the Earth. Beyond the ionosphere is the exosphere which gradually fades off into space.

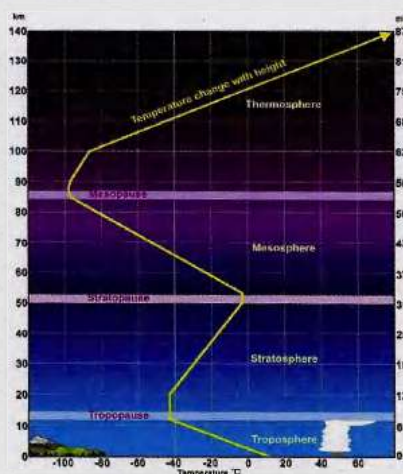


Fig. 41.2

An average temperature profile through the layers of the atmosphere.



CFCs AND THE OZONE LAYER

Chlorofluorocarbons (CFCs) are man-made compounds that contain only atoms of carbon, chlorine, and fluorine. They were developed in the 1920's as alternatives to the toxic sulphur dioxide and ammonia refrigerants used at the time. They have also been used as aerosol propellants, electronic cleaning solvents and to produce the bubbles in styrofoam. CFCs are ideal for these and other applications because they are cheap, chemically inert, non flammable, have low toxicity and can be readily converted from a liquid to a gas and vice versa.

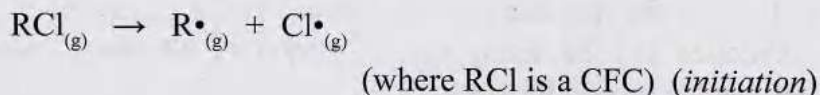
The main CFCs were derivatives of methane and ethane. They are denoted by the industry nomenclature CFC-11 (trichlorofluoromethane - CFCl_3), CFC-12 (dichlorodifluoromethane - CF_2Cl_2), CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane - $\text{C}_2\text{F}_3\text{Cl}_3$)



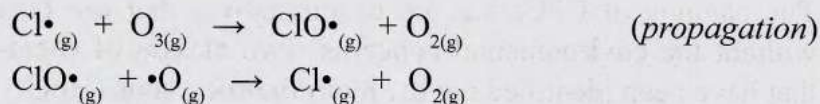
CFC refrigerants

CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane - $C_2F_4Cl_2$) and CFC-115 (chloropentafluoroethane - C_2F_5Cl).

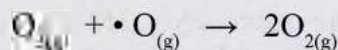
The production and use of CFCs grew enormously over the years which resulted in large emissions into the atmosphere. In 1974 it was discovered that CFCs accelerated depletion of the ozone layer in the stratosphere. Since they are chemically inert, they have a long lifetime in the atmosphere. They remain unchanged in the troposphere but when they reach the stratosphere, they dissociate in the presence of ultraviolet light into chlorine free radicals.



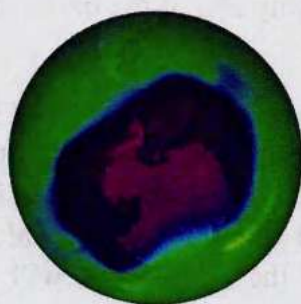
The chlorine free radicals then set off a chain reaction which converts ozone into oxygen.



The overall equation for the destruction of ozone is

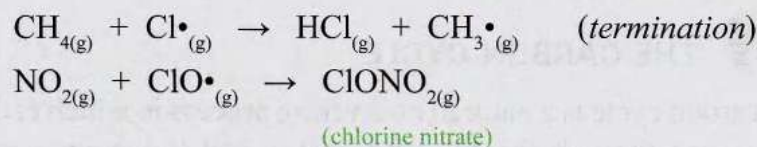


Since the chlorine free radical is reformed in the second reaction, one chlorine atom can destroy thousands of ozone molecules before it is removed from the stratosphere.



The Antarctic ozone hole

Chlorine-containing free radicals can be removed from the stratosphere by reacting with methane or nitrogen dioxide.

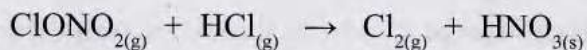


Normally, these two reactions would quickly remove the chlorine-containing free radicals from the stratosphere. However, in the





polar region hydrogen chloride and chlorine nitrate can react in the presence of ice particles to form chlorine and nitric acid crystals.

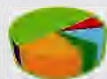


These remain in the stratospheric clouds until light intensities increase in the Arctic and Antarctic during spring. Then the chlorine dissociate into chlorine free radicals which result in severe depletion of the ozone layer in these regions.

Following the discovery of the “hole” in the ozone layer over Antarctica in 1985, many nations signed the Montreal Protocol designed to protect the ozone layer by phasing out the production of a number of substances believed to be responsible for ozone depletion.

The banning of CFCs has led to alternatives that can be used without the environmental concerns. Two classes of chemicals that have been identified are the hydrofluorocarbons (HFCs) and the hydrochlorofluorocarbons (HCFCs). HFCs do not contain chlorine and therefore cannot damage the ozone layer. HCFCs contain chlorine and can damage the ozone layer. However, the presence of hydrogen in the molecule makes them react with chemical species in the troposphere (e.g. hydroxyl radicals) leading to a shorter atmospheric lifetime. This greatly reduces the chance of the chlorine reaching the stratosphere. Thus HCFCs have approximately only 5% of the ozone depletion potential of CFCs.

In subsequent amendments to the Montreal Protocol, the HCFCs have been classified as transitional substances and they are scheduled for a phase-out. Although emissions of CFCs around the world is reduced due to international control agreements, the CFCs already in the atmosphere will continue to damage the ozone layer for many years. Scientists predict that the ozone layer would begin to recover in a few years and will be fully restored by the year 2050, if the implementation of the Protocol is continued.



THE CARBON CYCLE

The carbon cycle is a naturally occurring process in which carbon is recycled through the air, land, water, and living organisms. Large amounts of carbon exist in the atmosphere as carbon dioxide (CO₂). The main source of carbon dioxide is from

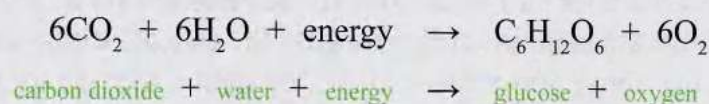


aerobic respiration of living organisms. This process involves the oxidation of carbohydrates to provide energy for the organisms.



Carbon dioxide is also released into the atmosphere through decay of organic matter, volcanic activity and when carbon compounds such as limestone are decomposed. Another important source of carbon dioxide in the atmosphere is from combustion. Human activities involving the combustion of fossil fuels and natural combustion processes such as forest fires also release carbon dioxide.

The main process which removes carbon dioxide from the atmosphere is photosynthesis. In this process green plants convert atmospheric carbon dioxide into organic molecules in the presence of light. Photosynthesis is the reverse of aerobic respiration.



Carbon dioxide is also removed from the atmosphere when it dissolves into surface water. Since more than two thirds of the surface of the Earth is covered with water, the oceans play a major role in maintaining the concentration of carbon dioxide in the atmosphere. The solubility of carbon dioxide in water increases when pressure increases but it decreases when temperature increases. In the oceans, aquatic animals use dissolved carbon dioxide to build their skeletons of calcium carbonate. These give rise to coral reefs and other limestone formations.

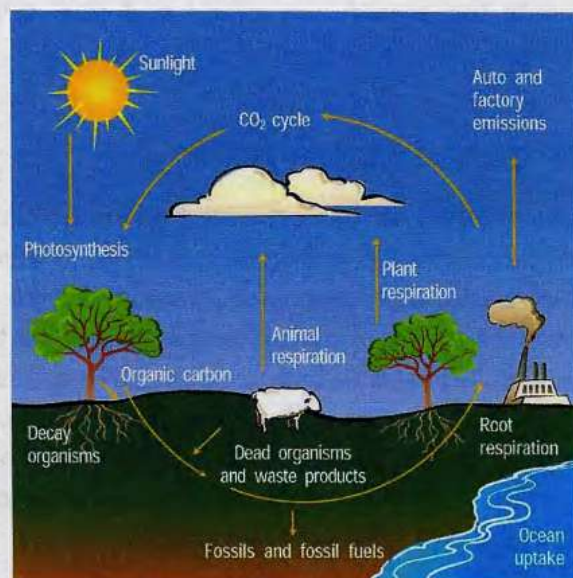


Fig. 41.3

The carbon cycle



Map of the Amazon rainforest

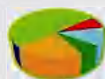


Combustion of fossil fuel

The Earth maintains a natural carbon balance. The sources which produce carbon dioxide in the air are balanced by **sinks** i.e. processes which remove it. Thus the composition of carbon dioxide in unpolluted air remains more or less constant. When concentrations of carbon dioxide are slightly altered, the system gradually readjusts to return it to its natural state. For example, when carbonic acid is removed from solution by weathering of rocks to produce carbon dioxide, the reaction adjusts by dissolving more carbon dioxide from the atmosphere to replace the carbonic acid used. This is a large-scale example of Le Chatelier's Principle.

Human activities such as deforestation and combustion of fossil fuels are significantly disrupting the natural balance of the carbon cycle. Clearing forest for industry and farming reduces the rate at which green plants remove carbon dioxide from the atmosphere by photosynthesis. Furthermore wood burning which occurs with forest clearance adds carbon dioxide to the atmosphere. In 1987, an area of the Amazon rain forest roughly the size of Britain was burnt, adding about 500 million tonnes of carbon dioxide to the atmosphere. The loss of the forests also meant that there were fewer trees to remove carbon dioxide from the air. Similar types of deforestation take place in Indonesia, India and some African countries.

Combustion of fossil fuels for electric power generation and transportation releases carbon dioxide into the atmosphere far more rapidly than it is removed. These activities lead to an overall increase in the concentration of carbon dioxide in the atmosphere. Since carbon dioxide is a greenhouse gas, this would tend to enhance the greenhouse effect and thus contribute to global warming.

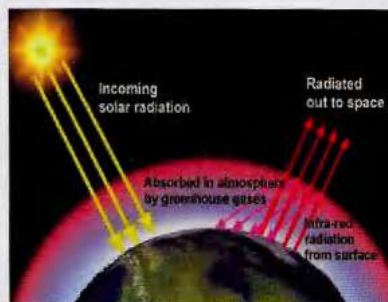


THE GREENHOUSE EFFECT

The greenhouse effect is the process by which certain gases in the atmosphere absorb infrared radiation to maintain the temperature of Earth. The process is compared with the way a greenhouse warms up by allowing sunlight to enter through its glass and prevent infrared radiation from leaving. Gases which absorb infrared radiation are called greenhouse gases. The main greenhouse gases in the atmosphere are water vapour, carbon dioxide and ozone. Other greenhouse gases include methane, nitrous oxide and the chlorofluorocarbons.



The atmosphere reflects about 30 % of solar radiation back into space. The other 70 %, which is mainly ultraviolet and visible light, penetrates the atmosphere and warms the Earth. The warm Earth radiates heat in the form of infrared radiation which is absorbed by molecules such as carbon dioxide and water in the atmosphere. These gases re-radiate most of the heat back to the Earth thus preventing the infrared radiation from escaping completely into space. This warms up the Earth and maintains an average global temperature of 15°C which makes life on Earth possible. Without this natural greenhouse effect, the average global temperature would be below -20°C.

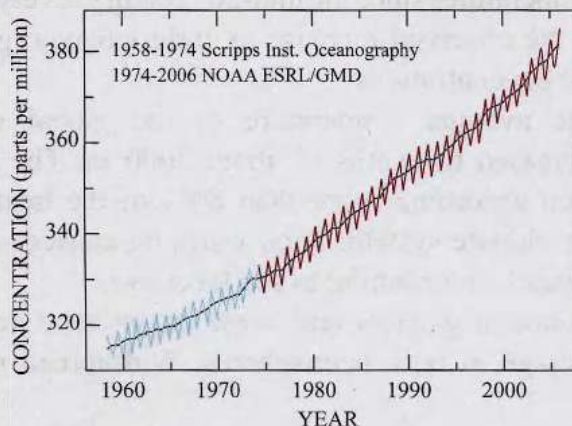


The greenhouse effect

The term “greenhouse effect” may be used to refer either to the natural greenhouse effect, due to naturally occurring greenhouse gases, or to the enhanced greenhouse effect which results from gases emitted as a result of human activities. In the last few centuries, human activities have increased the concentration of greenhouse gases in the atmosphere. Deforestation and combustion of fossil fuels for electric power generation and transportation have increased the amount of carbon dioxide in the atmosphere. Increasing quantities of methane are released from methane-belching cattle, decomposing landfills and wetlands such as rice paddies. Nitrogenous fertilizers which are used on most crops release nitrous oxide into the atmosphere. CFCs from refrigerants and aerosol propellants are extremely effective greenhouse gases. A CFC molecule is 10,000 times more effective in trapping heat than a carbon dioxide molecule. As more greenhouse gases are released in the atmosphere, more infrared radiation is absorbed thus enhancing the greenhouse effect. This then leads to an overall increase in the average global temperature.

Carbon dioxide concentration in the atmosphere has been increasing since measurements began in 1958 on Mauna Loa in Hawaii. Simultaneously, global temperatures have been rising.

Fig. 41.4 Atmospheric CO₂ at Mauna Loa Observatory





GLOBAL WARMING

Global warming refers to the average increase in the surface temperature of the Earth. This warming is largely attributed to the increase of greenhouse gases in the atmosphere which is caused by human activities such as burning of fossil fuels, deforestation and farming. The increase in concentration of greenhouse gases in the atmosphere enhances the greenhouse effect which increases the average global temperature.

The average global temperature has already increased about 0.6°C in the 20th century. This is the largest increase in surface temperature in the last 1,000 years and scientists are predicting an even greater increase over this century. Although the temperature change may sound small, it can trigger significant changes in climate. During the last Ice Age, 20,000 years ago, the Earth was roughly 5°C cooler than it is today. Since then it has warmed up, although not steadily, to the present temperature. That's roughly an increase of 1°C every 4,000 years. Current global warming scenarios predict a minimum of 1°C increase over this century.

In 2007, the Intergovernmental Panel on Climate Change (IPCC) reported that the emission of greenhouse gases from human activities significantly affects climate and unless it is modified, it will cause temperatures to rise by as much as 6.4°C by the end of the century. According to the IPCC, continued greenhouse gas emissions at or above current rates would cause further warming and would induce many changes in the global climate during the 21st century that would very likely be larger than those observed during the 20th century. Among those observed were:

- Eleven of the last twelve years (1995-2006) rank among the 12 warmest years in the instrumental record of global surface temperature since 1850.
- Most of the observed increase in globally averaged temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic greenhouse gas concentrations.
- The average temperature of the global ocean has increased to depths of about 3000 m. The ocean has been absorbing more than 80% of the heat added to the climate system. Such warming causes seawater to expand, contributing to sea level rise.
- Mountain glaciers and snow cover have decrease on average in both hemispheres. Widespread melting of



glaciers and ice caps has contributed to sea level rise.

- Global average sea level rose at an average rate of 1.8 mm per year over 1961 to 2003. The rate was faster over 1993 to 2003, about 3.1 mm per year.
- Average Arctic temperatures increased at almost twice the global average rate in the past 100 years.
- More intense and longer droughts have been observed over wider areas since the 1970s.
- Widespread changes in extreme temperatures have been observed over the last 50 years. Cold days, cold nights and frost have become less frequent, while hot days, hot nights, and heat waves have become more frequent.



The photograph taken in 1982, above, shows how the Upsala Glacier, part of the South American Andes in Argentina, used to look.

The ice on the Upsala Glacier today, shown in 2004 below, is retreating at least 180 ft. per year

Many scientists believe that global warming may lead to changes in precipitation and weather patterns. Warmer ocean water may result in more intense and frequent tropical storms and hurricanes. In September 1991 Japan was hit by Typhoon Mireille, its worst in 30 years. Then in September 1993 it was hit by Typhoon Yancy, the 13th that year and the worst in 50 years. Rising sea levels will increase flooding in coastal areas and river estuaries such as Bangladesh and the Nile Delta. London and many other British coastal cities will be threatened also. Decrease rainfall may increase drought and wildfires. Organisms that cannot survive in warmer environments may become extinct. Also it may result in a greater risk of heat stroke for individuals, and poor air quality.

Research suggests that as the Earth heats up, feedback mechanisms occur to enhance global warming. For example, the warm oceans will be less efficient in absorbing carbon dioxide, leaving more in the atmosphere and so adding further to global warming. Also large quantities of methane stored in the frozen tundra of the north and in the sea bed may be freed by rising temperature causing further warming. Another example is that as the temperature rises, more water will be evaporated from the oceans so providing more cloud which would enhance global warming.

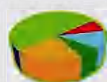


It is important to slow down global warming as much as possible. This can be achieved through energy conservation, using alternative pollution-free energy and reforestation. Some of the strategies proposed are policies for restrictions on big polluters, transportation management to reduce emissions from automobiles and to make better use of renewable energy sources such as solar power, wind power, and biodiesel.

Most Industrialized nations except the United States and Australia have ratified the Kyoto Protocol and agree to reduce worldwide greenhouse gas emissions to 5.2 % below 1990 levels between 2008 and 2012 with a shift to cleaner energies such as wind and solar power. The United States is a notable exception in that it releases more carbon dioxide than any other nation. Developing countries are not required to meet the emission standards in Kyoto. This includes China and India, the second and third largest emitters of carbon dioxide respectively.

Many environmental groups encourage individual action against global warming. Simple measures you can take in your everyday life to reduce global warming are given below.

- Choose reusable products instead of disposables.
- Buy energy-efficient products and use the energy-saving settings on your appliances.
- Replace regular light bulbs with compact florescent light (CFL) bulbs. CFL bulbs use two-thirds less energy, and give off 70 percent less heat.
- Conserve electricity by turning off lights, television, video player, stereo and computer when you're not using them.
- Explore your community's mass transit system and options for carpooling to work or school.
- Plant a tree
- Share information with others and encourage them to conserve.



COMBUSTION OF HYDROCARBON BASED FUEL

The main components of fossil fuels are combustible hydrocarbons. Complete combustion of the hydrocarbons produces carbon dioxide and water. However fossil fuels emissions contain several other pollutants due to impurities in the fuel. Fossil fuels used in power plants and vehicles are a major source of emission of carbon monoxide, nitrogen oxides, sulphur dioxide, and unburnt hydrocarbons.



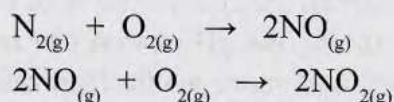
Carbon monoxide

Carbon monoxide (CO) is a colourless and toxic gas produced in vehicle exhaust when there is insufficient oxygen for complete combustion of hydrocarbon fuel in the engine. Carbon monoxide combines readily with haemoglobin in the blood to form the stable compound carboxyhaemoglobin. This makes the haemoglobin unable to transport oxygen which results in the cells of the body being deprived of oxygen. Exposure to carbon monoxide can cause headaches, dizziness and increase heart disease. A concentration as little as 400 ppm in the air can be fatal.

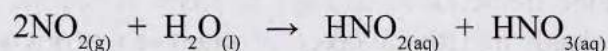
Carbon monoxide can also take part in a series of reactions which can lead to the increase in the level of tropospheric ozone. This ground-level ozone is a major component of smog. Exposure to elevated levels can lead to severe coughing, shortness of breath, lung and eye irritation.

Oxides of nitrogen

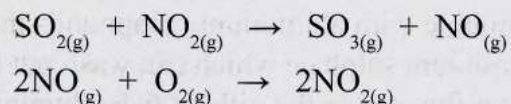
Oxides of nitrogen, collectively referred to as NO_x are produced when fossil fuels are burnt in air. Under normal conditions nitrogen and oxygen do not combine, however during combustion of fossil fuels, the high temperatures in engines or power plants provide sufficient energy for the nitrogen and oxygen molecules to react to form oxides of nitrogen. Nitric oxide (NO) which is the major form produced by combustion is oxidized in air to form nitrogen dioxide (NO_2).



Nitrogen dioxide reacts with water to form nitrous and nitric acid which fall as acid rain.



It also catalyzes the oxidation of sulphur dioxide to sulphur trioxide in the atmosphere.



The nitrogen dioxide is regenerated and the sulphur trioxide reacts readily with water in the atmosphere to form sulphuric acid which is the main cause of acid rain.



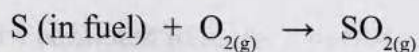
Combustion of hydrocarbon fuel in vehicles



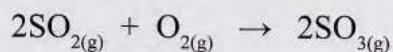
In addition, the sunlight-catalyzed reaction in the atmosphere between oxides of nitrogen and unburnt hydrocarbon leads to photochemical smog, a brown haze often seen above large cities. It is a respiratory irritant and can cause bronchitis and decrease resistance to respiratory infections.

Sulphur dioxide

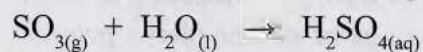
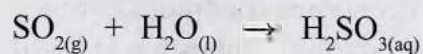
Sulphur compounds occur naturally in both coal and crude oil. The combustion of such fossil fuels in power stations is the main source of sulphur dioxide emission.



Sulphur dioxide is further oxidized to sulphur trioxide in the atmosphere.



Both sulphur dioxide and sulphur trioxide react with water in the atmosphere to form acid rain.



Acid rain

In an unpolluted atmosphere, carbon dioxide, the oxides of sulphur and oxides of nitrogen give rainwater a pH of about 5.5-5.0. In heavily industrialized areas, the concentration of these gases increases in the atmosphere and the pH of rain can reach as low as 4.0. This is about ten times more acidic than rain in unpolluted air. Rain which is more acidic than its natural value is referred to as **acid rain**.

Acid rain has done tremendous damage to trees in Europe and has caused the death of fish in lakes of many countries such as Canada, Sweden, the USA and UK. As acid rain percolates through soil, it leaches out essential nutrients required by plants resulting in loss of large areas of forest. Furthermore, the sulphate ions in acid rain can combine with aluminium compounds in the soil to form soluble aluminium sulphate which can wash out into lakes and rivers. As water flows over the gills of fish, aluminium hydroxide is precipitated on the gills. The gills secrete mucus and become clogged so preventing oxygen uptake. This results in the death of the fish.

Other effects of acid rain include:

- corrosion of metals in bridges, houses and vehicles
- destruction of limestone, marble and cement work on buildings
- destruction to trees and reduction in growth of many plants
- lowering the pH in lakes which results in the death of fish
- irritation to the respiratory system

Volatile organic compounds (VOCs)

Unburnt hydrocarbons are produced in vehicle exhaust when there is insufficient oxygen for complete combustion of the hydrocarbon fuel in the engine. Also volatile hydrocarbons, such as butane, evaporate from fuel tanks and filling stations on warm days. Thus transportation accounts for about half the total hydrocarbon emissions. **Volatile organic compounds (VOCs)** are often used interchangeably with hydrocarbon emissions. This term is broader and recognizes the fact that incomplete combustion of hydrocarbons may incorporate some oxygen in their structures and form compounds like aldehydes.

Some VOCs, such as benzene, are carcinogenic while others are respiratory irritants. Many pollutants are formed by atmospheric oxidation of hydrocarbons. These include aldehydes and irritating smog components such as peroxyacetylnitrate (PAN) and ozone.

Photochemical smog

The word 'smog' was initially used to describe the combination of smoke and fog which was found over cities where industries release large amounts of sulphur dioxide. The Great Smog of 1952 darkened the streets London and killed thousands of people. The Clean Air Act of 1956 reduced sulphur dioxide levels and made this kind of smog a thing of the past in London. However, a new kind of smog, known as photochemical smog, has developed. It is produced by the chemical reaction of sunlight, nitrogen oxides (NO_x) and volatile organic compounds (VOCs) from exhaust emissions in the atmosphere. It consists of a mixture of oxidizing substances such as ozone, nitrogen dioxide and peroxyacetylnitrate (PAN).

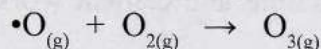
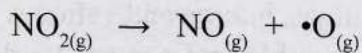
It is suggested that the production of ozone in the troposphere is formed when nitrogen dioxide dissociates in the bright sunlight into nitrogen oxide and oxygen atom, then the oxygen atom reacts



Smog over Mexico City

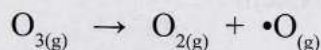


with molecular oxygen to form ozone.

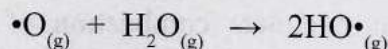


Once ozone is formed, it is believed that PAN is generated from a series of reaction.

Formation of an oxygen radical



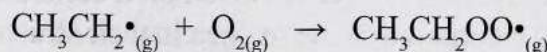
Formation of hydroxyl radicals



Formation of an ethyl radical



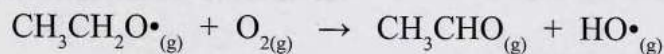
Formation of a peroxy radical



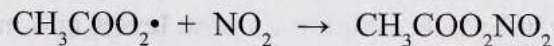
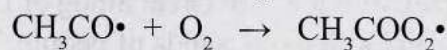
Oxidation of NO to NO₂



Oxidation to ethanal



Then



(PAN)

Photochemical smog is extremely irritating to the respiratory system. It is very prevalent when there is bright sunlight and heavy traffic. The brown haze characteristic of photochemical smog is mainly due to the presence of nitrogen dioxide.

Pollutants such as carbon dioxide (CO₂), carbon monoxide (CO), sulphur dioxide (SO₂) and nitric oxide (NO) are referred to as **primary pollutants**. These are produced directly from the combustion of fossil fuel itself. **Secondary pollutants** are formed as a result of subsequent reactions between these primary

pollutants and other exhaust emissions. Secondary pollutants include nitrogen dioxide (NO_2), ozone (O_3) and PAN.

Lead compounds

The addition of tetraethyl lead to gasoline reduces knocking, however, it releases lead compounds in exhaust emissions. Leaded fuel is being phased out in most countries due to an unacceptable amount of lead pollution in the environment. Lead is toxic and can enter the blood stream by inhalation or by ingestion directly or indirectly through the food chain. It slowly builds up over time in the body. It is associated with gastrointestinal problems, such as constipation, diarrhea, and vomiting. Chronic lead poisoning result in neurological problems such as reduced IQ, irritability, insomnia, excess lethargy or hyperactivity, headache and in extreme cases, seizure and coma. It is much more harmful to children than adults because it can affect children's developing nerves and brains. Leaded fuel is being replaced by unleaded high octane fuel.

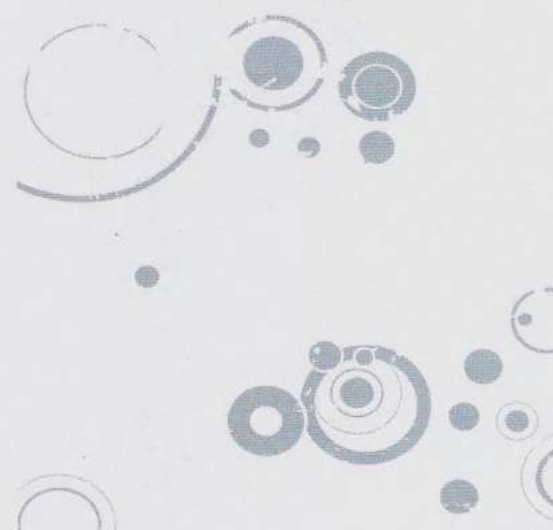
Particulate matter

Fossil fuel use also produces particulates such as dust, soot, smoke, and other suspended matter. These particles are respiratory irritants as they are small enough to penetrate into the lungs. Diesel fuel contains more carbon atoms per molecule than petrol so that diesel engines produce about fifty times more particulate matter than petrol engines.



THE NITROGEN CYCLE

The nitrogen cycle describes the circulation of nitrogen and nitrogen-containing compounds in nature. Nitrogen is used in biological processes to produce complex organic molecules like amino acids, nucleic acids and chlorophyll. Most organisms are unable to utilize nitrogen gas in the atmosphere although there is an abundant supply of it. The nitrogen in the air is fixed into forms usable by living organisms.



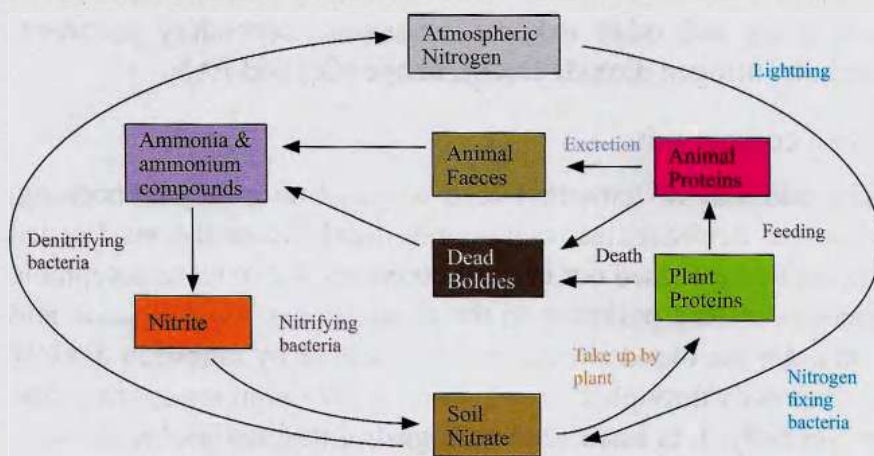
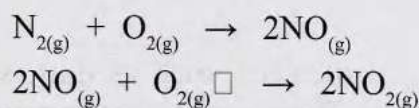


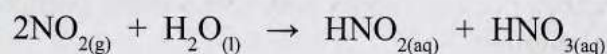
Fig. 41.5

The nitrogen cycle

Atmospheric nitrogen is fixed in nature either by lightning or by nitrogen fixing bacteria. During thunderstorms, the lightning provides sufficient energy for the nitrogen and oxygen molecules to react to form nitric oxide (NO) which is oxidized in air to form nitrogen dioxide (NO₂).



Nitrogen dioxide dissolves in rain to form nitrous and nitric acid.



When this rain falls to the earth it forms nitrates and nitrites in the soil.

Some nitrogen fixing bacteria live in symbiotic relationships (*Rhizobium* in the root nodes of leguminous plants), while others live free in the soil. They convert atmospheric nitrogen into ammonium ions which are used to make plant proteins. All plants however, can absorb nitrates from the soil which are used to make plant proteins. When plants are consumed by animals, plant proteins are converted to animal proteins.

The remains of plants and animals are decomposed into ammonium compounds and returned to the soil. The ammonium compounds are converted by nitrifying bacteria into nitrites and nitrates which plants can use again.

Denitrifying bacteria reduce nitrates and ammonium compounds in the soil into nitrogen gas which is released back into the atmosphere.

Human activities have altered the natural nitrogen cycle when nitrogen gas is removed from the air during combustion of fossil fuel by vehicles and industrial plants, by extensive cultivation of legumes and by the Haber process in the production of fertilizers.



CONTROL AND PREVENTION OF ATMOSPHERIC POLLUTION

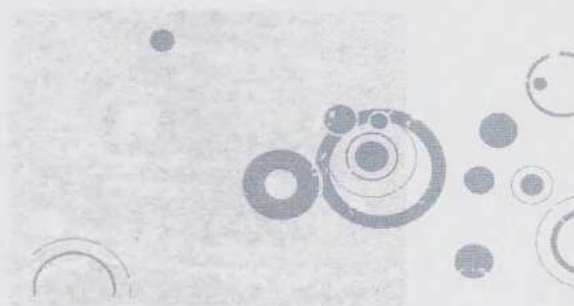
Our environment is being polluted to a large extent by industrialization and transportation. Presently over 80% of all the energy used by industrialized countries is fossil fuels. Fossil fuels are a non-renewable resource and the amount remaining in the Earth is limited. Existing technologies for new energy sources are promising but still there is a need to research and develop cleaner and more sustainable energy alternatives. Major changes are needed in industrialized countries to control and prevent atmospheric pollution. These include using alternative and cleaner fuels, improving mass transit systems and minimizing pollutants at its source with pollution control equipment.

Alternative fuels

Since there are concerns about air pollution and petroleum-dependence, new technologies for alternative and cleaner fuels are being researched. Many under development are only in their initial stages. Some alternative sources of energy are discussed below.

Nuclear energy

Nuclear fission can occur when a nucleus of a heavy atom captures a neutron or it can happen spontaneously. It produces energy for nuclear power plants. Uranium-235 and plutonium-239 are the most common nuclear fuels. When a uranium-235 nucleus is bombarded with a neutron, it splits into radioactive fragments and releases neutrons in the process. These neutrons then bombard other uranium-235 nuclei in a chain reaction producing a tremendous amount of heat energy. This energy, when let out slowly, can be harnessed to generate electricity. However if it is let out all at once, it can make a tremendous explosion as in an atomic bomb. In a nuclear reactor, the chain reaction is slowed down and controlled to produce readily available energy. Nuclear fission of 1 gram of uranium-235 can produce as much energy as that of burning 3 tonnes of coal. However, the waste products of nuclear fission are highly radioactive giving rise to a nuclear waste problem.



Another form of nuclear energy is called **nuclear fusion**. It involves the fusion of smaller nuclei into a heavier nucleus. The sun produces energy in this way by combining hydrogen nuclei into a helium nucleus. Nuclear fusion creates less radioactive material than nuclear fission and it is thought of as the path to unlimited energy. Scientists have been working on the extraction of "heavy" hydrogen (deuterium) from water and fusing it to form helium. However they are still encountering difficulty in controlling nuclear fusion and making a fusion reactor to produce electricity.

Ocean energy

Moving waves of the ocean have kinetic energy. This **wave energy** can be used to power a turbine which can turn a generator. Wave energy systems are usually very small and can be used to power a warning buoy or a small light house.

Another form of ocean energy is called **tidal energy**. At high tide, water is trapped in reservoirs behind dams. Then when the tide drops, the water behind the dam is allowed to fall through a height onto the blades of turbines which are connected to generators just like in a regular hydroelectric power plant. In order for tidal energy to work well, at least 16 feet between low tide and high tide is needed. There are only a few places where this tide change occurs around the Earth. The La Rance Station in France uses tidal energy to power over 240,000 homes.



The Open Cycle OTEC at Keahole Point, Hawaii Island.

The surface of the ocean absorbs solar energy and is warmer than the deep ocean water. **Ocean thermal energy conversion (OTEC)** uses this difference in temperature to generate electricity. The process involves pumping cold water from about 1 kilometre deep in the ocean to the surface and extracting energy from the flow of heat between the cold water and warm surface water. A difference of at least 20°C is needed between the warmer surface water and the colder deep ocean water to produce a significant amount of power. This type of technology is being demonstrated in Hawaii.

Solar Energy

Solar energy comes from the Sun. It can be used directly in crop drying, solar cooking and solar water heaters. Solar energy can also be used to make electricity. In the Mojave Desert in California, huge rows of highly curved mirrors are used to focus sunlight onto a pipe that gets hot enough to boil water which makes steam to turn a turbine to make electricity. This makes electricity for

more than 300,000 homes. The problem with solar energy is that it works only when the Sun is shining. Some solar plants use sunlight during the day but at night and on cloudy days, they burn natural gas to boil the water to continue to make electricity.

Solar or photovoltaic cells can convert solar energy directly into electricity. It is used for lights and small appliances such as calculators, refrigeration and air conditioning. It is also used to power electric cars and communication satellites. One suggestion for energy in the future is to put solar satellites in space. These would collect solar energy, convert it to electricity and transmit it to Earth. However scientific feasibility is not yet established.

Although solar energy does not release air pollution, it still has an impact on the environment. Solar energy involving the collection of solar rays through collectors needs large tracts of land as a collection site. This impacts the natural environment. Solar cells use the same technologies as the production of silicon chips for computers. The manufacturing process uses toxic chemicals which also has environmental impacts.

Wind energy

Farmers have been using wind energy for many years to pump water from wells and to turn large grinding stones to grind wheat or corn. Wind is also used to make electricity. When wind blows it spins the blades of a wind turbine which turns a generator to make electricity. If the wind gets too high, the turbines are designed with brakes that will keep the blades from turning too fast and being damaged.

Wind is blowing in many places all over the Earth. The only problem is that it is not windy all the time. For a wind turbine to work efficiently, wind speeds must be above 20 kilometres per hour to turn the turbines fast enough to generate electricity. California produces about 11% of the wind generated electricity used in the world. Denmark and Germany are other countries that use a lot of wind energy.

Harnessing wind energy also has its downside, mostly involving land use. Farms and cattle grazing could have used the same land under the wind turbines. Wind turbines could cause erosion in desert areas. They also affect the natural view because they tend to be located on or just below ridgelines. Bird deaths also occur due to collisions with wind turbines.



Photovoltaic 'tree' in Styria, Austria



Wind energy



Hydroelectric energy

Hydroelectric power uses the gravitational potential energy and kinetic energy in water to make electricity. Dams are built to collect water. As the water falls through a height, it spins the blades of turbines which are connected to generators which produce electricity. Hydroelectric power is found in the mountainous areas where there are lakes and reservoirs and along rivers. About 87 % of the electricity made in Washington is produced by hydroelectric facilities.

Environmental concerns are also associated with hydroelectric energy. These include people being displaced and prime farmlands and forests being flooded by dams. In addition, dams change the biotic and abiotic features of the river and the land downstream.

Geothermal Energy

Geothermal energy is the heat energy stored in rocks and fluids below the surface of the Earth. Naturally occurring geothermal vents reach the surface in areas where there are geysers and hot springs. Some of these areas have so much steam and hot water that it can be used to generate electricity. Holes are also drilled in the ground to reach the hot rocks below and then injected with water to produce steam. The steam is pumped through pipes and used to turn the blades of turbines which are connected to generators to make electricity.

Although geothermal power seems natural, it does have its limitations. Extraction of geothermal energy depends on the geography of the Earth. The rocks under the operating power plant must have permeable cracks and enough water or heat to turn the turbine. Also in the extraction of geothermal energy, hazardous substances such as hydrogen sulphide may come up from underground which can be difficult to safely dispose of.

Biomass

In terms of energy production, biomass is commonly referred to as plant material grown for use as biofuel. They can be harvested, dried and burnt, or further processed into liquid or gaseous fuels such as alcohols and biogas respectively.

Alcohols are commonly produced from biomass through fermentation. In Brazil, ethanol is produced from sugar cane and is used as an automotive fuel in alternative fuel vehicles (AFVs). In the United States it is produced from corn and is mostly used as a gasoline additive. A blend of 10% ethanol and 90% gasoline is sold as gasohol. Methanol can be combined with plant oils,



animal fats or recycled restaurant grease to make biodiesel which can be used as an additive or in its pure form in AFVs.

Biogas is produced by anaerobic decay of organic wastes, usually manure or garbage. Biogas consists mainly of methane and carbon dioxide. It can be produced in a biodigester where bacteria decompose organic wastes. Also it can be recovered from landfills and burnt to produce electricity.

Biomass as a fuel does not disrupt the carbon cycle. Carbon from the atmosphere is converted into plant material by photosynthesis. On decay or combustion the carbon goes back into the atmosphere. It is considered a renewable resource because the plants which make biomass can be grown over and over. Biomass fuel allows wastes to be reduced, reused and recycled in the environment. However, if the crops are not replanted, then biomass can release carbon dioxide that will contribute to global warming.

Fuel Cells

A fuel cell is an electrochemical cell which converts chemical fuel of a continuous supply into electrical energy. Chemical fuels used in fuel cells include hydrogen, natural gas, propane and methanol.

Hydrogen fuel cells use hydrogen and oxygen to produce electricity. They are pollution-free as water and heat are their by-products. They are used in spacecrafts to provide heat, electricity and drinking water for astronauts. Hydrogen fuel cells are a promising technology for future to use as fuel in vehicles and to provide power for homes and industries.

Hydrogen fuel has some limitations, in that, it is found on Earth combined with other elements such as carbon and oxygen. To use hydrogen, it must be separated from these elements. Hydrogen can be produced from the electrolysis of water or from the reforming of natural gas or light petroleum distillates. Also some algae and bacteria can use solar energy and make hydrogen under certain conditions. Another limitation is that hydrogen is difficult to store and distribute.

Mass transit

Mass transit or public transportation comprises of transport systems such as buses, trains and subways. It provides scheduled services on fixed routes taking passengers to their destinations without the need for automobiles. The essential feature of mass transit is that there are more people per vehicle which means less



In 2008 Honda Motor Co. Ltd. announced that the FCX Clarity fuel cell vehicle will serve as the official car of the 2008 Indy Japan event.



traffic congestion and reduced air pollution.

Although taking public transport is environmentally preferable to private transport, diesel buses are by no means cleaner burning vehicles. In Los Angeles, diesel engines for transit buses have been outlawed and the federal government has enacted particulate reduction standards that should have been met by 2007. New buses running on alternative fuels such as ethanol, propane, biodiesel and natural gas are entering the market and improving the environmental appeal of public transportation. The emissions of soot and the pollutants that cause smog from these alternative fuels are 40 percent below those of the diesel buses. However, they are less impressive in reducing global warming since they reduce emissions of greenhouse gases by only 5 to 10 percent. Electric buses are also in the early market stage and produce zero emissions.



London Underground, the oldest rapid transit system in the world.

Construction of separate infrastructure can make public transport faster than on public roads. For example, buses that travel on public roads are generally slower than private transport because of the initial wait for a bus, frequent stops, and traffic congestion. In urban areas, rapid transit systems such as trains and subways usually transport large amounts of people at high frequency and are totally independent of other traffic. These forms of transportation are fast and efficient. They use electric power which is quieter and do not pollute the transport passages. Mass transit rarely covers its operating costs through fares and generally relies on government subsidies.

Pollution control technology

Sequestering

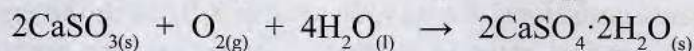
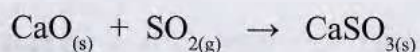
Fossil fuels will remain the main source of energy well into the twenty-first century. Predictions of global energy use suggest that the concentration of carbon dioxide will continue to increase in the atmosphere unless major changes are made. **Sequestering** is a technique that can be used to capture and store carbon dioxide and other greenhouse gases in stable compounds so that they will not be released into the atmosphere. For example, carbon dioxide can be trapped by metallic oxides to produce stable carbonates. Sequestering can be used at large fossil fuel energy facilities to reduce carbon dioxide emissions at its source. Although sequestering increases the running costs of the power plant significantly, carbon dioxide emissions can be reduced by up to 90%. Natural sequestration also occurs during photosynthesis when plants trap carbon dioxide from the atmosphere and



incorporate it into biomass.

Scrubbers

Scrubbers are another group of devices that control gaseous emissions, especially acidic gases such as SO_2 and HCl . Scrubbers remove or neutralize pollutants from flue gases (exhaust gases that are conveyed from a furnace to the atmosphere via a chimney) or from other gas streams. Scrubbing involves addition of an alkali, a basic oxide or a carbonate into the gas stream to react with the acidic gases. For example, calcium oxide and calcium carbonate can be used as scrubbing reagents to react with sulphur dioxide to form calcium sulphite which can be oxidized by air to form calcium sulphate.



Hydrated calcium sulphate (gypsum) can be used in plaster-board and cement manufacture.

Washers

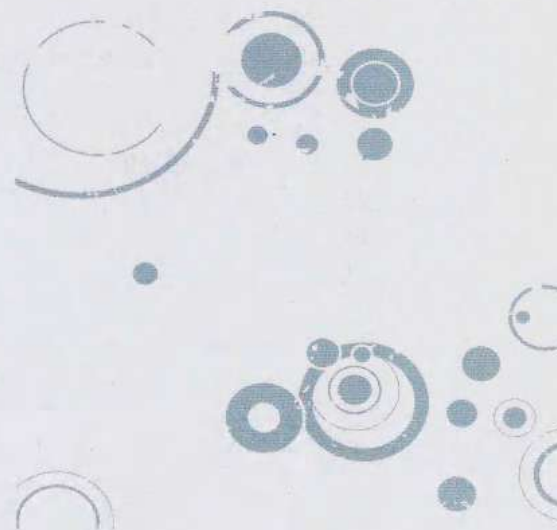
Air washers are used to remove volatile vapours and dust from exhaust fumes. Pollutants are removed by dissolving in a solvent such as water. An elaborate spray system creates a mist of water in which the air must pass through. As the air comes in contact with water droplets, dust and volatile vapours dissolve in the water and remain behind.

Filters

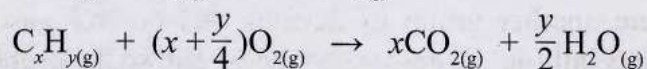
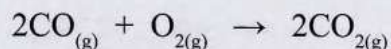
Filters are also used to separate dust particles from air. Filters use the principle of particle sizes to clean air. Larger particles cannot pass through the filter and will remain behind while the smaller air particles will flow through. Air filters are used in engines such as internal combustion engines and gas turbines. Electrostatic precipitators are highly efficient filtration devices and can easily remove fine particulate matter such as dust and smoke from the air stream using an induced electrostatic charge.

Catalytic converters

A catalytic converter is fitted to a vehicle exhaust system to reduce pollutant gases from emissions. It consists of a mixture of platinum and rhodium catalyst coated on to a honeycomb filter which maximizes the surface area on which the catalyzed reactions take place. Carbon monoxide and unburnt hydrocarbon



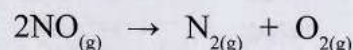
are oxidized to carbon dioxide.



Both nitrogen monoxide and carbon monoxide are removed at the same time in a redox reaction.



New catalytic converters can reduce nitrogen monoxide to nitrogen and oxygen.



A three-way catalytic converter removes carbon monoxide, nitrogen monoxide and unburnt hydrocarbon simultaneously from exhaust emissions. An oxygen sensor is fitted to the engine since exact air-fuel ratio is needed to carry out the reactions efficiently. Also the converter is placed near the engine so that it heats up quickly because the catalyst does not start working until it reaches a temperature of about 200°C . In addition, the catalyst is poisoned by lead so vehicles have to use unleaded fuel.

Catalytic converters have made a remarkable difference in the reduction of pollutant in vehicular exhaust fumes. For example, since catalytic converters were installed in automobiles in the United States in 1975, carbon monoxide concentrations in the atmosphere have decreased by about 40% even though the number of cars has doubled in the United States.





Questions

1. Explain the following terms:
 - (a) green-house effect
 - (b) global warming
 - (c) photochemical smog
 - (d) acid rain
2.
 - (a) With the aid of relevant equations, explain how the concentration of ozone is maintained in the atmosphere.
 - (b) Why is the ozone layer important to life on Earth?
 - (c) How does CFCs affect the ozone layer?
 - (d) What are the consequences of increased destruction of the ozone layer?
3.
 - (a) Explain the importance of the carbon cycle.
 - (b) Discuss the role of the following in maintaining a balance of carbon dioxide concentration in the atmosphere:
 - (i) photosynthesis
 - (ii) respiration
 - (iii) combustion
 - (c) Identify one human activity that disrupts the balance of carbon dioxide concentration in the atmosphere.
 - (b) Discuss the consequences of increasing carbon dioxide concentration in the atmosphere.
4. Complete combustion of the hydrocarbons produces carbon dioxide and water. However fossil fuels emissions contain several other pollutants due to impurities in the fuel. Discuss the effects of the following products of combustion of fossil fuels:
 - (a) carbon monoxide
 - (b) sulphur dioxide
 - (c) lead compounds
 - (d) volatile organic compounds
5. Explain how the following can control atmospheric pollution:
 - (a) alternative fuel
 - (b) mass transit
 - (c) scrubbers



Solid waste is the solid materials that are generated from activities of living things and are discarded as useless or unwanted. Before the industrial revolution, the major constituents of solid waste were biodegradable domestic sewage and agricultural residues. These were decomposed and recycled in the soil. However with industrialization, the quality and quantity of the solid waste have changed. Waste from industrialized areas includes domestic waste, commercial waste, construction and demolition waste, industrial waste and hospital waste. Often these discarded waste materials can be reduced in the environment by reusing and recycling them. Solid Waste Management is about managing the waste in a manner that meets public health and environmental concerns.



REDUCE, REUSE AND RECYCLE

Reducing waste means lessening the amount of items consumed and discarded. It includes purchasing items that use minimum raw materials in production, have a longer life and can be used again after its original use. Reducing the amount of waste generated is a method of waste management that goes a long way toward protecting the environment.

Reusing an item means extending the life of the item after its original use instead of discarding or throwing it away. Empty jars can be reused as storage containers, broken products can be repaired and old toys or magazines can be donated to charity. Reusing items are even better than recycling because the items do not need to be reprocessed before they are used again. Reusing items reduces waste.

Recycling means processing materials from old used items that would otherwise become waste products. Materials like glass, metal, plastics, and paper are collected, separated and sent to facilities that can reprocess them into materials that can be reused. Recycling has a number of advantages which include conserving energy, reducing the consumption of natural resources and reducing the amount of waste that would have gone into landfills.

Waste reduction

In recent times the rate at which solid waste is generated has slowed down as a result of waste reduction processes such as reusing and recycling materials. Some waste materials which can be recycled are glass, paper, plastics and metals.



RECYCLING GLASS

Some glass bottles are returnable and are cleaned and reused a number of times before recycling. Other used glass containers can be collected at recycling centers. They are cleaned and sorted by colour. Once the glass is separated, it is crushed in a glass processor. The crushed glass, called **cullet**, is melted down and added to soda ash (Na_2CO_3), limestone and sand. The mix is heated to form molten glass which is blown or molded into new glass containers.

Glass is 100 percent recyclable. It can be continually recycled without losing its quality. Glass recycling efforts mainly focus on glass bottles and jars because these make up the larger percentage of the glass that is thrown away. Light bulbs, ceramics, glass mirrors and windowpanes are not recycled with glass because they are not made with the same materials as glass jars and bottles.

In preparing glass containers for recycling, the lids or caps must be removed and the containers must be rinsed with water. Labels can be left on since they will burn up when the glass is melted. The glass must be separated by colour before recycling because coloured cullet cannot be used to make clear glass.

New glass is made from soda ash, limestone and sand. Cullet melts at a lower temperature than these raw materials and saves about half the energy normally required for making glass from all new materials. Soda ash, limestone and sand are cheap raw materials but quarrying for these materials impacts on the environment. Every tonne of cullet used in the manufacturing process saves about 1.2 tonnes of raw materials.



Mosaic of stained glass



RECYCLING PAPER

Paper is the number one material that is thrown away. Most paper is made from trees that have been cut and pulped. Although paper companies plant trees specifically for papermaking, recycling paper reduces the number of trees used to make paper. For every tonne of paper made from recycled paper, 20 to 30 trees are saved.



Recycling paper reduces energy usage by about 50 %, air pollution by about 70% and water pollution by about 35%. It also reduces land pollution by keeping paper products out of landfills.

In preparing waste paper for recycling, materials such as food, plastic and metals must be removed. The paper is then sorted into different grades such as cardboard boxes, newspapers, and office paper. The different grades are used to make different types of recycled paper products.



Recycled paper

The paper to be recycled is placed in a pulper with water. The pulper chops the paper into small pieces. Eventually the paper is converted into a slurry mixture called **pulp**. The pulp is pushed through screens with holes of various sizes to remove particles that are larger than the pulp fibers. Printing ink and sticky materials like adhesives are then removed by a step called **de-inking**. In this step air bubbles and a surfactant are passed through the pulp slurry which cause the ink and sticky materials to collect as foam on the surface of the pulp. Removing the foam leaves clean pulp behind. The pulp is bleached if white paper is required. The clean pulp is made into paper products either by using the recycled fiber alone, or by mixing it with new wood fiber.

Making the paper involves diluting the pulp mixture with water and spraying it onto a wire screen which is moving quickly through a paper machine. The water drains from the pulp on the screen and the fibers rapidly bond together to form a sheet. The sheet is pressed to remove more water and then dried. Paper is sometimes clay coated to give it a smooth, glossy finish for printing.

Paper is only recycled about 5-7 times because the fibers get shorter and weaker in the process. New wood fiber is often mixed with the used paper to improve strength. In 2005, a record 51.5% of the paper consumed in the United States was recovered for recycling, that was about 51 million tonnes of paper products.



RECYCLING PLASTICS

Reusing plastic is preferable to recycling as it uses less energy and reduces demands for raw materials. Plastic crates, containers and other products can be reused for many years before recycling.

Plastics tend to be more complicated to recycle than glass and paper because there are many different types of plastics each requiring a different method of handling in the recycling process. Recycling different types of plastics together can produce recycled plastic



with unpredictable properties. Plastics carry a resin identification code and must be sorted before they are recycled.

Plastic containers should be washed and squashed. Labels can be left on the containers but caps should be removed as they are usually made from a different type of plastic from the containers. The plastic is chopped into flakes and heated under pressure to melt. It is filtered through a fine screen to remove any contaminants. The molten plastic is formed into strands, cooled and then cut into pellets. The recycled plastics pellets can be used to make plastic products such as flowerpots, carpets or moulded into containers again.

Although new plastic is produced from petroleum, it is more profitable for manufacturers to use new plastic than recycled plastic. The cost of new plastic is about 40 percent lower than that of recycled plastic. So while most people expect plastic to be recycled, consumers are not prepared to pay more for recycled plastic products.



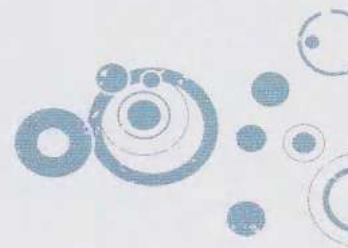
RECYCLING METALS

Scrap metal can be recycled indefinitely without losing any of its properties. Scrap metal is divided into ferrous and non-ferrous metals. Ferrous metal is scrap iron and steel while non-ferrous metal is scrap metal other than iron and steel. Aluminium, copper, zinc, nickel, chromium, silver and gold are some examples of non-ferrous metals. Ferrous metal can be separated from non-ferrous metal using magnets. Aluminium and steel are used in large quantities and create a waste disposal problem. Recycling these metals saves energy and reduces the waste going to landfills. Metals like gold, silver and copper have recognized value and are rarely discarded.

Aluminium

Recycling aluminium uses only about five percent of the energy needed to extract aluminum from bauxite. It is the most cost-effective material to recycle. The aluminium is collected and taken to a treatment plant where it is sorted and cleaned for reprocessing. Materials like steel, plastics, paper and dirt are removed as these can disrupt the recycling process.

The aluminium is shredded into small pieces and hot air is blown through it to remove the coatings and inks that may be present on it. The shreds are then melted in a furnace to produce molten





Aluminium cans are collected to be recycled.

aluminium. The molten aluminium is made into large blocks called ingots. The ingots are sent to mills where they are rolled out to make aluminium products such as cans, chocolate wrapping and other packaging. In as little as 6 weeks, recycled aluminium is ready to be used again.

Over 50% of aluminium cans are recycled worldwide. In the UK aluminium cans are recycled by Alcan where old cans are melted down and turned into ingots of aluminium which are used to make new cans. This is referred to as closed loop recycling since old cans go in and metal to make new cans comes out.

Steel

It is more energy efficient to use steel scrap to make new steel than to mine the iron ore and reduce it in a blast furnace. It takes about 60 percent less energy to make steel from recycled materials than it does from iron ore. Steel scrap is collected and easily separated from other waste using magnets.

Recycling steel is similar to aluminum recycling. Steel scrap is cleaned and melted in a furnace. It is then poured into casters that roll and flatten the steel into sheets. Recycled steel can be made into new cars, appliances, girders for buildings, or new steel cans. Like aluminum, steel does not lose any of its properties in the recycling process.

Recycling reduces the energy required for mining and refining processes. It also reduces the consumption of natural resources. For example, every tonne of recycled steel saves about one tonne of iron ore, 500 kg of coal and 20 kg of limestone. Products made from recycled materials save resources for future generations and reduce pollution.



IMPACT OF SOLID WASTE ON TERRESTRIAL ENVIRONMENT

The disposal of solid waste is a worldwide problem that continues to increase with population growth and industrialization. Although there are many different methods of disposing of solid waste, there is no absolutely safe way to do so.

Biodegradable and non-biodegradable

Natural products like paper and cardboard which are made from plant materials are **biodegradable** and break down easily in the environment and are recycled in nature. However materials such



as metals, glass and plastics which are used to make everyday products like electronic components, cans, glass containers and plastic packaging are **non-biodegradable**. These products do not break down easily and exist for a long time in the environment. For example, plastics take over 500 years to decompose and can accumulate in the environment.

New technologies are being used to make biodegradable plastics. Starch-based plastics are made by incorporating starch into the plastic so that it can be broken down by bacteria. Oxo-biodegradable plastics are made by introducing a degradable additive into the manufacturing process so that degradation of the plastic starts immediately after manufacturing. The additive reduces the plastic to a level which allows microorganisms to decompose it. The service life of the plastic can be controlled at the time it is manufactured which can range from a few months to many years. Researchers are also working on ways to make plastics more biodegradable from exposure to sunlight since many plastics break down when exposed to the sun for prolonged periods.

Land-filling

The most common method of solid waste disposal is land-filling. This may involve open dumping or using sanitary landfills. Large quantities of solid waste are disposed of by dumping into old quarries, coastal marshlands and other economical landfill sites.

Open dumping is cheap and disposes of large quantities of waste, however it looks unsightly, smells foul and attracts insects and rodents that spread diseases. Furthermore, water percolating through waste produces a black liquid called **leachate** which contains partly decomposed organic matter and toxic heavy metal ions that can pollute surrounding groundwater. Decomposing waste also releases methane which may be explosive. Since there are public health concerns with open dumps, efforts have been made to dispose of waste using sanitary landfills.

Sanitary landfills are different to dumps in that they are built to contain the waste. The bottom of the landfill is lined with impermeable layers and has a leachate collecting system which collects and treats the leachate before discharging it into the environment. The waste is spread in thin layers over the landfill site, then compacted and covered with soil to encourage bacterial decomposition and to keep away insects and rodents. The landfill also has a gas collecting system where methane produced can be



Sanitary landfill



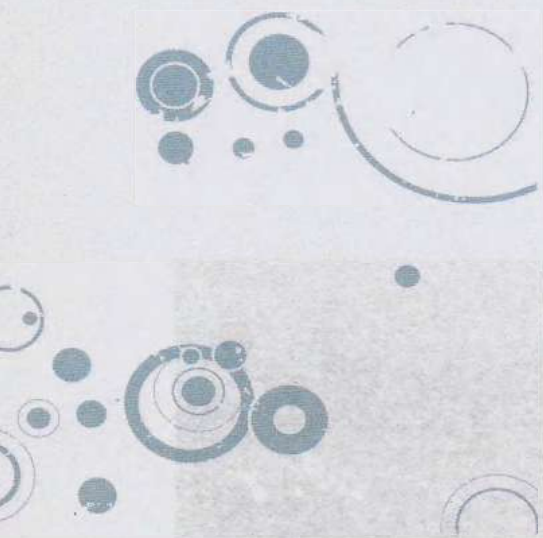
collected and used as a fuel.

After the landfill is exhausted it is covered and monitored for about 20 years before it can be used for other purposes such as recreation. Some potential problems with sanitary landfills include high start up cost, non-biodegradable materials filling the site too quickly and improper management of landfill which may cause water pollution from leachate and explosions from escaping gases.

Incineration

Incineration is another common method of solid waste disposal. It involves the combustion of waste at high temperatures. Incineration is more expensive to dispose waste than landfills but it is safer in that it destroys pathogens and converts toxic heavy metals to their oxides which are less harmful. Furthermore, the burnt ash takes up much less space than the solid waste itself. Incineration is used in countries such as Japan where land for waste disposal is not available. Modern incinerators can convert waste into heat energy which can be used to produce steam to generate electricity. Waste-to-energy incineration is being used extensively in Sweden and Denmark.

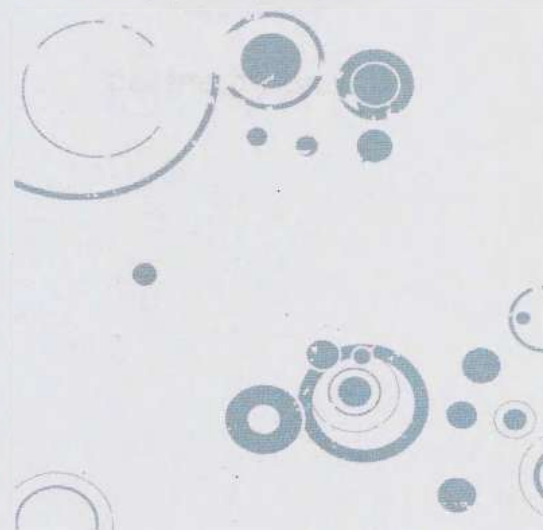
Incineration produces hazardous air pollutants such as carbon monoxide, oxides of sulphur and oxides of nitrogen in addition to a large amount of carbon dioxide and particulate matter. These emissions can be controlled by scrubbers, electrostatic precipitators and filters. However the burning of organic waste materials containing chlorine such as PVC has the potential to form a group of compounds called dioxins which is carcinogenic. Dioxins are formed at temperatures around 500°C but above 800°C in the presence of enough oxygen their formation can be avoided. Careful temperature regulation of incinerators is necessary to prevent the formation of dioxins when plastics are burnt.





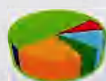
Questions

1. Explain the following terms:
 - (a) reduce
 - (b) reuse
 - (c) recycle
2. Describe how the following materials are recycled:
 - (a) paper
 - (b) glass
 - (c) metals
 - (d) plastics
3. Solid waste disposal is a problem that continues to increase with population growth and industrialization. Discuss the advantages and disadvantages of the following methods of solid waste disposal:
 - (a) open dumping
 - (b) sanitary landfills
 - (c) incineration



Green chemistry emerged from a variety of ideas and research in an effort to increase attention to problems of chemical pollution and resource depletion. *Green chemistry can be defined as the design of products and processes that minimize the use and generation of hazardous substances.* It applies across the life cycle of a chemical product from its design, manufacture, use, and eventual disposal. Green chemistry is also referred to as sustainable chemistry.

In 1998 Paul Anastas and John Warner co-authored the book, *Green Chemistry: Theory and Practice* that outlined the 12 principles of Green Chemistry which help to explain what the definition means in practice.



THE 12 PRINCIPLES OF GREEN CHEMISTRY

1. **Prevent waste:** Design chemical syntheses that will leave no waste to treat or clean up. It is better to prevent waste than to treat or clean up waste after it is formed.
2. **Maximize atom economy:** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Design less hazardous chemical syntheses:** Design synthetic methods to use and generate substances with little or no toxicity to either humans or the environment.
4. **Design safer chemicals and products:** Design chemical products that are fully effective yet have little or no toxicity.
5. **Use safer solvents and reaction conditions:** The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be avoided wherever possible. If they must be used then use safer ones.



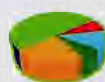
6. **Increase energy efficiency:** Carry out chemical reactions at room temperature and pressure whenever possible.
7. **Use renewable feedstock:** A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable. The source of renewable feedstock is often agricultural products or the wastes of other processes whereas the source of depleting feedstock is often fossil fuels or mining materials.
8. **Avoid chemical derivatives:** Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.
9. **Use catalysts,** not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are effective in small amounts and can carry out a single reaction many times. The more specific a catalyst is for a reaction, the less likely is the generation of waste products. In contrast stoichiometric reagents take part in the reaction, are used in excess and carry out a reaction only once.
10. **Design chemicals and products to degrade after use:** Design chemical products to break down to harmless substances after use so that they do not accumulate in the environment.
11. **Analyze in real time to prevent pollution:** Design analytical methods to monitor each step of the synthesis for the presence of pollutants and control the formation of these pollutants or their release into the environment.
12. **Minimize the potential for accidents:** Design chemicals to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.





EXAMPLES OF GREEN CHEMISTRY

The wide range of applications of green chemistry includes uses in the pharmaceutical industry, as well as new approaches that reduce or eliminate the use of solvents, or render them safer and more efficient. Green chemistry has also inspired a growing number of ways to synthesize traditionally petroleum-based chemicals from biological materials. Green chemistry also plays a role in alternative energy and new ways to make solar cells, fuel cells, and batteries for storing energy.



PHARMACEUTICALS

The pharmaceutical industry seeks to develop medicines with less harmful side effects and using processes that produce less toxic waste. It uses green chemistry to restructure production processes, reduce environmental impact of drugs and their metabolites and minimize toxic chemicals used in reactions.



Januvia used to treat diabetes

The drug Simvastatin is used to treat high cholesterol. Professor Yi Tang, of the UCLA, devised an improved synthesis process using an engineered enzyme and low-cost feedstock. The previous process used hazardous chemicals and released large amounts of toxic waste. The company Codexis took the new mechanism and optimized the enzyme and synthesis process so the drug could be manufactured more safely, less expensively, and with less of an environmental impact.



Ibuprofen painkillers

Sitagliptin is the active ingredient in Januvia, a treatment for type 2 diabetes. The company Merck reduced the number of reaction steps in the Sitagliptin synthesis from eight to three, leading to an equally dramatic reduction in the amount of chemicals and solvent needed and the amount of waste generated. The revised synthesis increased the overall yield of Sitagliptin by nearly 50% and reduced the amount of waste by more than 80%.

The chemical company BASF now makes its annual output (about 2 billion tablets) of the painkiller ibuprofen in a three-step rather than a six-step process. About 77% of the atoms which are mostly derived from hydrocarbons used in the synthesis make it into the final product compared to 40% before.



The chemotherapy drug paclitaxel which is marketed as Taxol was originally made by extracting chemicals from yew tree bark, a process which used a lot of solvent in addition to killing the tree. The drug is now made by growing tree cells in a fermentation vat. This reduces the amount of solvent used in extracting the chemicals from the tree and the amount of waste produced.



GREEN SOLVENTS

According to the fifth principle of green chemistry the use of auxiliary substances such as solvents should be avoided wherever possible and safe when used. Solvents are used in high volumes and are typically volatile organic compounds (VOCs). There is the potential for large amounts of waste, air pollution, and other health concerns. Finding safer alternatives or removing solvents altogether is one of the most effective ways to impact the safety and efficiency of a process or product. An analysis done between 2004 and 2013 indicated that the U.S. drug industry's use of chemicals dropped nearly by half and the reduction was largely due to using less organic solvent.

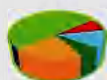
DuPont and Genencor International developed a bio-based process to make 1,3 – propanediol. The chemical is used as a solvent, stabilizer, and enzyme carrier. It is made from microorganisms like the E. coli bacteria that are genetically modified to use sugars from crops in a fermentation-based process. 1,3 – propanediol is used in the environmentally friendly cleaning brands like Method and Seventh Generation. These brands also use another green solvent ethyl levulinate glycerol ketal. This solvent is made through a chemical process which converts the ligno-cellulosic materials from low cost biomass, such as corn cobs, sugar cane bagasse, or paper mill sludge to levulinic acid. The main role of this solvent is to make the fragrance oils soluble and keep the overall cleaning formula stable, rather than to dissolve soil or grease. Other green solvents seeing increasing use are supercritical carbon dioxide, and ionic liquids.

Polystyrene foam is a common material used in packing and food transportation. Dow Chemical discovered that supercritical carbon dioxide worked well as a blowing agent and allowed the polystyrene to be more easily recycled. Traditionally, CFC and other hazardous chemicals were used in the production. The CO_2 used in the process is reused from other industries.



Green solvents

DyeCoo Textile Systems recently invented an industrial-scale, water-free dyeing process and equipment that uses supercritical carbon dioxide, which functions like a liquid when under pressure and at slightly elevated temperature. Traditional dyeing required about 7 gallons of water to dye a T-shirt in addition to energy to dry the dyed material.



BIO-BASED PLASTICS

The innovation to develop plastics that are made from renewable, biodegradable sources reduces our dependence on petroleum products, protects humans and wildlife from undesirable chemicals in old plastics, and reduces waste and impact on the environment.



Bio based plastic

NatureWorks in Minnesota, makes food containers from a polymer called polylactic acid branded as Ingeo. Plants like corn or cassava capture and sequester CO_2 transforming it into glucose molecules. The glucose is converted to dextrose by enzymes and then fermented into lactic acid. The lactic acid is transformed into rings of lactides and then polymerized into the polylactide polymer called polylactic acid (PLA). The biopolymer is used in packaging and can be clear, opaque, flexible or rigid. It is similar to polystyrene and exhibits tensile strength comparable to petroleum-based thermoplastics. Ingeo plastics are recyclable and compostable.

Recycling can provide economically viable, true closed-loop, cradle-to-cradle solutions to zero waste. However, identifying Ingeo bioplastic in the recycle stream is the challenge.

DuPont and Genencor International developed a bio-based process to make 1,3 - propanediol (PDO), the monomer for DuPont Sorona® polymer. Microorganisms like the E. coli bacteria were genetically modified to use sugars from crops in a fermentation-based process to produce 1,3 - propanediol. The PDO polymer can be used to make textile, carpet and packaging. This bio-based method uses less energy, reduces emissions, and employs renewable resources compared to traditional petrochemical processes.



BASF is commercially producing renewable 1,4-butanediol (1,4-BDO). This bio-based material is used to produce the Ecoflex compostable polyester film, which is used together with cassava starch and calcium carbonate to create fully biodegradable Ecovio bags. These bags disintegrate into carbon dioxide, water and biomass in industrial composting systems.

PAINTS

Green chemistry goes beyond eliminating lead from paint. It reduces toxic volatile organic compounds (VOCs) that are released from the paint and uses safer pigments. Sherwin-Williams developed water-based acrylic alkyd paints made from recycled plastic bottles (PET), acrylics, and soybean oil. These paints combine the performance benefits of alkyds and cut the VOC content by 60%. In manufacturing the new paint formula, Sherwin-Williams used 320,000 pounds of soybean oil, 250,000 pounds of PET, and eliminated 1,000 barrels of oil. This technology has the potential to eliminate millions of pounds of VOC emissions while supporting the recycling of multi-million pounds of PET each year.

COMPUTER CHIPS

Computer chips require many chemicals, large amounts of water and energy to manufacture. In a study conducted in 2003, the industry estimated it took 630 times the weight of the chip in source materials to make one chip. Scientists have developed a process that uses supercritical carbon dioxide in one of the steps of chip preparation, and it significantly reduces the quantities of chemicals, energy, and water needed to produce chips.

The poultry industry leaves behind billions of pounds of waste feathers annually. Feathers can be processed into a low-grade animal feed, incinerated or buried. Feed processing requires water and energy, incineration requires emission control and ash disposal while burying involves storage and handling. Richard Wool found a way to use chicken feathers to make computer chips. The protein, keratin, in the feathers was used to make a fibre form that is both light and tough enough to withstand mechanical and thermal stresses. The feather-based printed circuit board works at twice the speed of traditional circuit boards. Although this technology is yet to be used commercially, the research has led to the use of feathers as a source material for biofuel.



Eco friendly paint



ALTERNATIVE ENERGY



Perovskite solar cells

To replace silicon-based photovoltaic cells, which are relatively expensive and require a lot of energy to make, scientists have turned to the perovskite and quantum dots solar cells. A perovskite is made up of a lead or tin halide-based material as the light-harvesting active layer. Perovskite materials such as methylammonium lead halides are cheap and simple to manufacture. However there are concerns that this technology is not really “green” as it uses hazardous metals. A quantum dot solar cell uses nanocrystals of semiconductor materials as the absorbing photovoltaic material. It emits a bright glow of a pure colour when they are excited by light or an applied voltage. Some quantum dots solar cells can use cadmium or perovskite-based semiconductors.

Power from fuel cells is cleaner, generating less than 1% of the amount of pollution produced by traditional power production. The technology has the potential to increase energy efficiency, reduce greenhouse gas emissions and reduce air pollution compared with traditional combustion engines. Fuel cells are still too expensive and experimental to be practical for widespread use. However, they are currently used to power city buses, NASA spacecraft and wastewater treatment plants. In wastewater treatment facilities these cells convert waste methane gas, or biogas, generated from sludge decomposition into useful electricity.

Batteries provide a reliable source of stored chemical energy. However, batteries contain a number of metals such as cadmium, nickel and lead which can be toxic in the environment. The lithium-ion batteries are considered safe for landfills or incinerators. However, there is still an issue with billions of these batteries being thrown away in landfills rather than being recycled. The lithium ion battery has a high energy capacity for its low mass, which makes it very suitable for mobile devices such as laptop computers and mobile phones. Also vehicle makers can extend their vehicles range without excessive mass. However challenges with lithium ion battery include expensive cost of production and the risk of explosion during transportation and use. Lithium ion is being combined with nanotechnology to significantly reduce cost and improve recycling.



Researchers in America have developed a virus which can latch onto and coat itself with inorganic materials like cobalt turning each virus strand into a tiny length of wire. Together these nano-wires form compact and powerful battery components. The viral battery basically grows itself in water and it is biodegradable.

Research

Scientific research utilizes a number of techniques that use hazardous chemicals and release waste into the environment. The principles of green chemistry can be employed to make these techniques safer, cheaper, and less wasteful. Life Technologies developed a three-step, one-pot synthesis method for polymerase chain reaction (PCR), used in genetic testing. The new process is more efficient, consuming up to 95 percent less organic solvent and releasing up to 65 percent less waste compared with the conventional protocol. Using the new process, Life Technologies eliminates about 1.5 million pounds of hazardous waste each year.



IMPACT OF GREEN CHEMISTRY

Concerns for climate change, depletion of the ozone layer and effects of mining and drilling can be addressed through the development and implementation of green chemistry technologies. Green chemistry is effective in reducing the impact of chemicals on living organisms and the environment. Many environmental laws and regulations target hazardous chemicals but green chemistry seeks to reduce waste materials, hazards, risks, energy and cost, making it easier for companies to comply with the law.

Many chemicals such as pesticides and industrial emissions end up in the environment. Green chemistry allows for the breakdown of chemicals to harmless products or the recovery of waste for further use. It results in cleaner air and water for organisms as less waste and hazards are released into the environment. It lowers the potential for global warming, ozone depletion and smog formation. Green chemistry also provides safer food as toxic chemicals which can enter food chains are reduced or eliminated. Plants and animals thus suffer less harm from reduced toxic chemicals in the environment and less chemical disruption of ecosystems.



In the chemical industry, green chemistry offers increased safety for workers. Since there is less use of toxic materials, there is less potential for accidents and less need for personal protective equipment. Fewer synthetic steps allows for faster manufacturing of products and reduced cost. Using renewable feedstock decreases the use of petroleum products thus reducing the concerns of drilling, mining and depletion of fossil fuel. Green chemistry attends to the problem of hazard at the design and process level which result in higher efficiency, less waste, better product quality, and reduced liability.



Green chemistry is a branch of chemistry that focuses on the design of products and processes that minimize the use and generation of hazardous substances. It is a multidisciplinary approach that involves chemists, engineers, and environmental scientists. The goal is to create a sustainable chemical industry that is safe for workers and the environment, and that uses renewable resources and minimizes waste.

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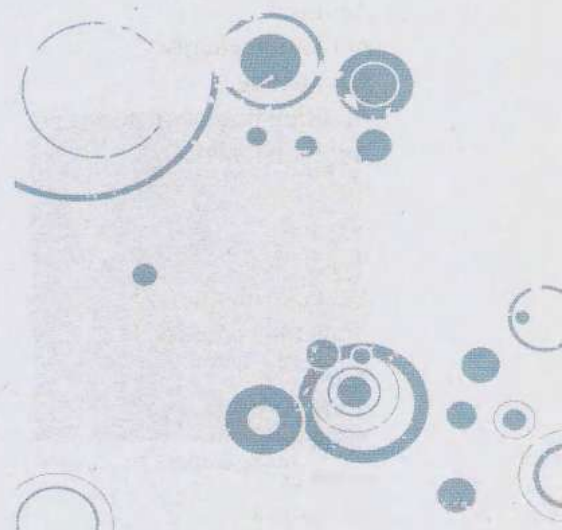
Questions

1.
 - (a) Define green chemistry.
 - (b) State five principles of green chemistry.
 - (c) Give an example of the use of green chemistry in the following:
 - (i) pharmaceuticals
 - (ii) alternative energy
 - (iii) plastics
 - (d) What is the impact of green chemistry on living things and the environment?
2. Green chemistry aims to
 - (a) Utilize non-renewable energy
 - (b) Design chemical products and process that maximize profits
 - (c) Design chemical products and processes that work most efficiently
 - (d) Design safer chemical products and processes that reduce or eliminate the use and generation of hazardous substances
3. Which of the following are among the 12 Principles of Green Chemistry?
 - (a) Re-use waste
 - (b) Use only new solvents
 - (c) Design commercially viable products
 - (d) Use catalysts, not stoichiometric reagents
4. Industrial benefit(s) of green chemistry include
 - (a) Innovating new products to entice customers
 - (b) Greater awareness with environmental legislation
 - (c) Reduced costs associated with waste treatment and disposal
 - (d) All of the above



5. Which of the following is the greenest solvent?
- (a) Water
 - (b) Ethanol
 - (c) Methanol
 - (d) Benzene
6. Environmental benefits of green chemistry include
- (a) Reduced raw materials and natural resources used
 - (b) Cheaper production technologies and more emissions
 - (c) Larger quantities of hazardous waste to be treated and disposed of
 - (d) All of the above
7. Lignin, grass, and cellulose are all types of
- (a) Monomers
 - (b) Enzymes
 - (c) Bio-based feedstock
 - (d) Anti-cancer compounds
8. _____ is an excellent 'green' solvent as well as a greenhouse gas.
- (a) Ethanol
 - (b) Methanol
 - (c) Carbon monoxide
 - (d) Carbon dioxide
9. Soybean is used to replace traditional inks in printer cartridges. This is an example of which green chemistry principles?
- (a) Atom economy
 - (b) Reduce derivatives
 - (c) Increase energy efficiency
 - (d) Use of Renewable Feedstock
10. Bio-polymer is an example of which Green Chemistry Principle?
- (a) Catalysis
 - (b) Prevent waste
 - (c) Design for degradation
 - (d) Safe solvents and auxiliaries

11. The use of solar power is an example of which Green Chemistry Principle?
- (a) Atom economy
 - (b) Increase energy efficiency
 - (c) Design safe chemicals
 - (d) Less hazardous synthesis
12. An example of green chemistry is
- (a) Bio-plastics
 - (b) Recycled carpet
 - (c) A sublimation reaction
 - (d) A product made on Earth Day
13. Green chemistry can NOT reduce which of the following?
- (a) Cost
 - (b) Waste
 - (c) Awareness
 - (d) Risk & Hazard



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